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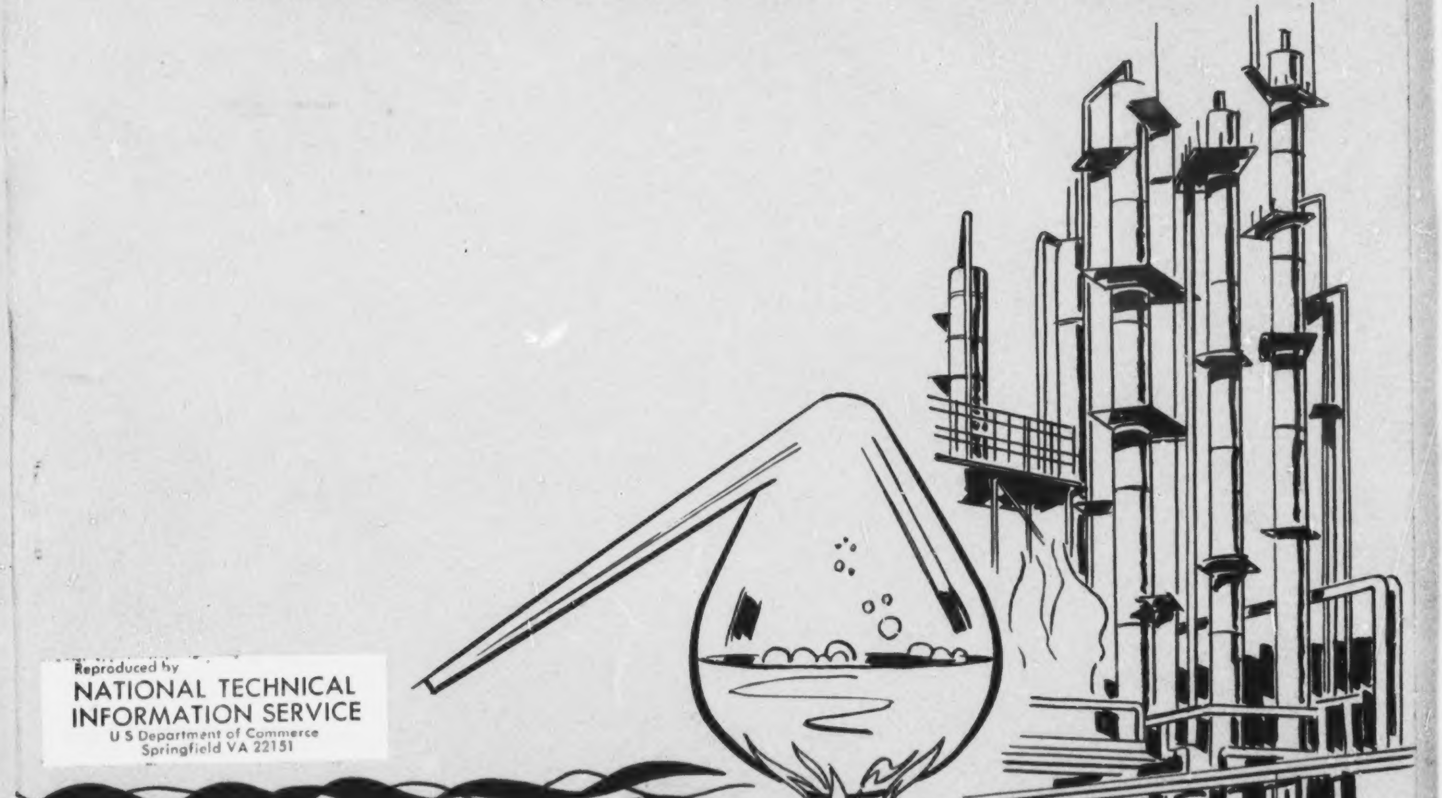
# Preliminary Investigational Requirements - Petrochemical and Refinery Waste Treatment Facilities



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# "PRELIMINARY INVESTIGATIONAL REQUIREMENTS - PETROCHEMICAL AND REFINERY WASTE TREATMENT FACILITIES"

prepared by

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for the

WATER QUALITY OFFICE

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# ABSTRACT

The objectives of this report include the compilation, interpretation, and presentation of the pertinent aspects which constitute a preliminary wastewater treatability study for the refining and pretrochemical industries. The preliminary investigation relative to the successful treatment of petrochemical and refinery wastewaters should include those factors essential in the proper development of design criteria for pollution abatement and control facilities.

The wastewater survey is the basis from which a treatability study can be developed, and necessarily includes locating, analyzing, and properly interpreting the nature of pollutional sources within a petrochemical or refinery complex. This includes normal process and utility effluent, contaminated storm runoff, ballast water discharge, and other related sources of wastewater. Each of these wastewaters must be properly characterized with respect to their organic and inorganic constituents. This characterization schedule is designed to best determine the impact of the particular waste stream on the treatment facility and the receiving body of water. In-plant control of wastewaters is an integral part of any survey as the elimination or sequestering of pollution at the source is often the most economical approach toward resolving the problem.

The treatability study, whether it involves chemical, biological, or physical treatment, must necessarily be programmed to yield definitive information concerning pollutional removal rates, anticipated levels of residual or non-removable constituents, and treatment process requirements. Translating bench or pilot scale data to prototype design then must incorporate proper scale-up factors.

The overall project of evaluating the treatability of a wastewater is predicated on the assimilation of sufficient information from which the optimal selection of treatment processes can be made. Given manpower and cost constraints in view of this objective, the scope of any treatability study must be carefully planned and properly implemented.

This report was submitted in fulfillment of Contract No. 14-12-588 between the Federal Water Quality Administration and Engineering-Science, Inc.

Key Words: Treatability, wastewater characterization, organic and inorganic constituents, bench scale or pilot scale studies, scale-up, correlation of organic parameters, screening procedures.

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16. Abstract

Case studies indicate that locating, analyzing, and properly interpreting the nature of pollutional sources within a petrochemical or refinery complex is the basis from which a treatability study can be developed. Each of the wastewaters including normal process and utility effluent, contaminated storm runoff, ballast water discharge, and other related sources of wastewater, must be properly characterized with respect to their organic and inorganic constituents. The treatability study must be programmed to yield definitive information concerning pollutional removal rates, anticipated levels of residual or non-removable constituents, and treatment process requirements. The overall project of evaluating the treatability of a wastewater is predicated on the assimilation of sufficient information from which the optimal selection of treatment processes can be made. (Smith-Texas)

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# GLOSSARY OF TERMS

Adsorption -- The adherence of dissolved, colloidal, or finely divided solids on the surfaces of solid bodies with which they are brought into contact.

Aeration -- The bringing about of intimate contact between air and a liquid by one of the following methods: Spraying the liquid in the air; bubbling air through the liquid; or by agitation of the liquid to promote surface absorption of air.

Alkalinity -- A term used to represent the content of carbonates, bicarbonates, hydroxides, and occasionally borates, silicates, and phosphates in water. It is expressed as parts per million of calcium carbonate.

Bacteria, Aerobic -- Bacteria which require free (elementary) oxygen for their growth.

Bacteria, Anaerobic -- Bacteria which grow in the absence of free oxygen and derive oxygen from breaking down complex substances.

Basin, equalization -- A basin employed to even out irregularities in flow and constituent concentration.

Biochemical Oxygen Demand (BOD) -- A utilization of organic materials by bacteria expressed in terms of oxygen demand.

Chemical Oxygen Demand (COD) -- A measure of the oxidation of organics using potassium dichromate as the oxidant.

Carbon, Activated -- Carbon particles usually obtained by carbonization of cellulosic material in the absence of air and possessing a high adsorptive capacity.

Coagulation -- The agglomeration of colloidal or finely divided suspended matter by the addition to the liquid of an appropriate chemical coagulant, by biological processes, or by other means.

Flocculation -- The formation of small gelatinous masses in a liquid by the addition of coagulants or through biochemical processes or by agglomeration.

Flotation -- A method of raising suspended matter to the surface of the liquid in a tank as scum -- by aeration, by the evolution of gas, chemicals, electrolysis, heat, or bacterial decomposition -- and the subsequent removal of the scum by skimming.

Lagoon, Sludge -- A relatively shallow basin, or natural depression, used for the storage or digestion of sludge, and sometimes for its ultimate detention or dewatering.

Liquor -- Water, sewage, and industrial wastes, or any combination of the three.

Liquor, Mixed -- A mixture of activated sludge and sewage in the aeration tank undergoing activated sludge treatment.

Nitrification -- The oxidation of organic nitrogen into nitrates through biochemical action.

Outfall -- The point or location where sewage or drainage discharges from a sewer, drain, or conduit.

Oxygen, Dissolved -- Usually designated as D.O. The oxygen dissolved in sewage water or other liquid usually expressed in parts per million or percent of saturation.

Period,Aeration -- The theoretical time, usually expressed in hours, that the mixed liquor is subjected to aeration in an aeration tank undergoing activated sludge treatment; is equal to (a) the volume of the tank divided by (b) the volumetric rate of flow of the sewage and return sludge.

Sedimentation -- The process of subsidence and depositon of suspended matter carried by water, sewage, or other liquids, by gravity. It is usually accomplished by reducing the velocity of the liquid below the point where it can transport the suspended material.

Sedimentation, Final -- Settling of partly settled flocculated or oxidized sewage in a final tank.

Seeding, Sludge -- The inoculation of undigested sewage solids with sludge that has undergone decomposition, for the purpose of introducing favorable organisms, thereby accelerating the initial stages of digestion.

Sludge, Activated -- Sludge floc produced in raw or settled sewage by the growth of zoogleal bacteria and other organisms in the presence of dissolved oxygen, and accumulated in sufficient concentration by returning floc previously formed.

Sludge, Conditioning -- Treatment of liquid sludge preliminary to dewatering, and to facilitate dewatering and drainability, usually by the addition of chemicals.

Sludge, Dewatering -- The process of removing a part of the water in sludge by any method, such as draining, evaporation, pressing, centrifuging, exhausting, passing between rollers, or acid flotation, with or without heat. It involves reducing from a liquid to a spadable condition rather than merely changing the density of the liquid (concentration) on the one hand or drying (as in a kiln) on the other.

Sludge, Digested -- Sludge digested under anaerobic conditions until the volatile content has been reduced, usually around 50 percent.

Sludge, Primary -- Sludge obtained from a primary settling tank.

Sludge, Process -- A biological sewage treatment process in which a mixture of sewage and activated sludge is agitated and aerated. The activated sludge is subsequently separated from the treated sewage (mixed liquor) by sedimentation, and wasted or returned to the process as needed. The treated sewage overflows the weir of the settling tank in which separation from the sludge takes place.

Solids, Suspended -- (1) The quantity of material deposited when a quantity of water, sewage, or other liquid is filtered through an asbestos mat in a Gooch crucible. (2) The solids that either float on the surface of, or are in suspension, in water, sewage, or other liquids; and which are largely removable by laboratory filtering.

Solids, Volatile -- The quantity of solids in water, sewage, or other liquid lost on ignition of the total solids.

Tank, Aeration -- A tank in which sludge, sewage, or other liquid is aerated.

Tank, Final Settling -- A tank through which the effluent from a trickling filter, or aeration or contact aeration tank flows for the purpose of removing the settleable solids.

Tank, Flocculating -- A tank used for the formation of floc by the agitation of liquids.

Tank, Mixing -- A tank or channel so designed so as to provide a thorough mixing of chemicals introduced into liquids.

Tank, Surge -- A water tank employed to absorb irregularities in flow.

Total Organic Carbon (TOC) -- Concentration of organic material as expressed in terms of total organic carbon.

Total Oxygen Demand (TOD) -- Oxygen demand as measured using automated total combustion techniques.

Treatment, Primary -- removal of settleable solids.

Treatment, Secondary -- Treatment, by biological methods, generally activated sludge, to remove BOD from a waste.

Treatment, Tertiary -- Treatment, generally by activated carbon sorption, to remove residual COD after secondary treatment.

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# CONCLUSIONS

The following conclusions are based on a review of treatability study and preliminary investigative requirements.

1. The trend of recent refinery and petrochemical complex construction has been toward the emphasis of oil recovery from oily waste streams, separation of high and low organic wastewaters, in-plant control, and water reuse. Treatability studies and preliminary engineering considerations should be directed toward the continuance and enhancement of this philosophy.

2. The characteristics of wastewaters discharged from refinery and petrochemical complexes depend on the age of the facility, the nature and source of the crudes processed, the design and type of production facilities, the cooling water requirements, and the degree of in-plant housekeeping and control practiced. Generally, wastewaters from refineries tend to have more uniform characteristics than the more complex and diverse liquid wastes discharged from petrochemical facilities.

3. Wastewater surveys should be designed so as to classify wastewater sources with respect to oily and non-oily substances, inorganic and organic contaminants, high TDS and low TDS waters, and sanitary discharges. A survey, so oriented, assures a more practical engineering solution.

4. Sampling points and frequencies should be consistent with the "pollution potential" of the station in question. Batch process operations normally require more frequent sampling than do continuous process operations. Areas from which waters containing high concentrations of pollutants are discharged should be sampled frequently enough to provide statistically reliable information.

5. The survey should include flow measurements at critical points not only to serve as a basis for compositing samples but also for establishing critical base flow patterns within the complex. Moreover, such information is necessary for calculating total pollutional loads discharged.

6. The quality and quantity of storm runoff should be obtained for major storms which occur during the wastewater survey period. If this is not possible, runoff information should be synthesized as accurately as possible.

7. Wastewater surveys should include estimates of contaminants emanating from sources other than storm or process discharges, such as ballast handling areas, truck dump areas, sources of pipeline leaks, tank farms, and areas from which accidental spills commonly occur.

8. Analyses should be performed as close to the source as possible. If this cannot be done, samples collected during the survey phase should be carefully preserved until the necessary analyses can be performed. Refrigeration without freezing, freezing, and acidification are the methods most commonly used. Selected confirmatory analyses should be performed to insure that the integrity of the sample has been maintained between the time of sampling and testing.

9. An analytical program should be designed in order to best describe critical pollutants. Inorganic analyses are rather well defined, although organic analyses often are more difficult to interpret. The BOD test is subject to many limitations, particularly when estimating the organic content of refinery and petrochemical wastewaters. The COD test is limited to a lesser extent such as resistance of some compounds to chemical oxidation and chloride interference. However, TOC and TOD analyses can be used to effectively supplement BOD and COD data for proper organic interpretation.

10. The BOD/COD or BOD/TOC ratio of untreated refinery or petrochemical wastewaters is indicative of the degree of biological treatment obtainable. The possibility of physical or chemical methods of treatment should be considered when the BOD/COD ratio is in the range of 0.1-0.4.

11. As effluent criteria imposed by the various regulatory authorities become more stringent, water reuse will become more attractive. Attention should be given this possibility when conducting surveys and treatability studies so that the necessary information can be integrated into engineering designs.

12. There is no standard format for conducting wastewater surveys or treatability studies. At present, such projects are conducted by consulting engineers, equipment manufacturers, and industrial personnel, either individually or collectively. This results in many diverse approaches toward the development of problem solutions. Regardless of the entity conducting the survey and treatability study, a more uniform, but flexible, format should be established.

13. Many petrochemical and refinery waste treatment facilities have and are being built without the benefit of adequate survey and treatability data. In many instances, this results in the discharge of an effluent of lower quality than permitted with the consequent loss of time and money to the industrial facility. The regulatory authorities can encourage the practice of more extensive pre-construction survey and treatability studies through treatment process requirements.

14. The pilot or bench scale approach to developing design criteria is better documented for primary and secondary conventional treatment processes than for tertiary treatment. Generally, the larger the scale of the test unit processes, the more accurate the data when compared to full-scale operating information.

15. To date, little scale-up information from pilot or bench scale to full-scale units is available. This lack of information can result in the overdesign or underdesign of treatment systems, even if an accurate survey has been performed and a comprehensive treatability study has been conducted.

16. Three general levels of personnel are required to perform wastewater surveys and treatability studies. These include project managers or specialist-type consultants for project management and data interpretation, project supervisors responsible for the day-to-day implementation, and technical assistants to perform routine operations and analysis.

17. Although many of the larger petrochemical and refinery industries conduct surveys and treatability studies in-house, consulting engineers and equipment manufacturers will continue to be responsible for a major portion of this effort.

18. Costs for conducting surveys and treatability studies depend on the quality, quantity, and pattern of flow of the wastewaters. The complexity and age of the petrochemical plant or refinery also influence this cost. Directly, the costs are related to the type of personnel utilized, the number of analyses to be performed, the pilot or bench scale equipment required, and the complexity of resolving the data. In many cases, budgetary considerations constrain the scope of the survey and the treatability study. This constraint may result in subsequent capital losses attributed to overdesign, operational surcharges, etc.

19. Comprehensive surveys and treatability studies for petrochemical and refinery facilities are an integral part of the preliminary analytical and engineering phases leading to optimum implementation of project pollution control programs. Economic benefits in both construction and operation can result from the optimization of design which is possible when such data is available to the designer.

## RECOMMENDATIONS FOR

## IMPROVING TECHNOLOGY OF PRELIMINARY INVESTIGATION REQUIREMENTS

A review of this treatise, developed from experience in the field and from case histories cited in the literature, leads to the following recommendations. These include suggestions for improving technology of preliminary investigation requirements necessary for successful pollution abatement programs in the petrochemical and refining industries:

1. The quality of wastewater discharged from standard process units within a refinery such as crude units, catalytic cracking units, coking units, utility areas, etc., can be categorized with respect to major contaminants. Therefore, attempts should be made to survey and statistically report data available from operating refineries. Such information would greatly enhance the programming of wastewater surveys in refineries where this information is not now available as well as provide some design bases for treatment facilities serving refineries not yet constructed. It is recognized that such a tabulation should be limited to "standard" production units. Applicable characterization parameters for each "standard" unit also should be listed.

2. Particular emphasis should be given to the development of a monitoring and alarm system within a refinery or petrochemical complex. This includes the detection of specific substances resulting from batch dumps or spills which adversely affect treatment process efficiencies and/or the biology of the receiving environment. Such substances include specific organics, refractory hydrocarbons, heavy metals, etc.

3. As more treatability studies are performed and documented and treatment facilities constructed therefrom, more sophisticated scale-up factors should be defined. This is particularly true when considering biological and chemical-physical treatment systems. This can be achieved by obtaining operating data from the bench, pilot, and full-scale units and analyzing and relating the data statistically.

4. A more comprehensive evaluation of the impact of storm flow runoff on treatment facilities and surrounding areas should be included in any wastewater survey. This information then should be included in the treatability evaluations if such flow is judged to significantly influence test system responses.

5. A better-defined bench or pilot scale approach for simulating and determining the effects of occasional pollutional discharges such as those from ballast handling areas to a treatment system should be developed.

6. The design of continuous flow wastewater treating processes should always be based on data developed from continuous reactor treatability studies. Semi-continuous or batch reactor studies should only be conducted when a similar operation is expected of the full-scale system. When carefully interpreted, studies made using batch and semi-continuous reactors can serve as screening tests for detecting toxicity, or for roughly estimating continuous flow process performance.

7. It is recognized that sludge handling and disposal facilities may constitute a significant portion of both construction and operating costs for a petrochemical or refinery waste treatment plant. These sludges include oily sludges, chemical sludges, or excess biological sludges. Consequently, an integral and important part of the treatability study should be the development of data to allow intelligent selections and accurate sizing of processes for handling these sludges.

8. There is a need to develop a rational and more uniform approach toward bench or pilot scale analysis of tertiary treatment processes, particularly as more tertiary plants are put into operation providing operational data available for treatability evaluation.

9. A more uniform approach in conducting surveys and treatability studies is suggested through the preparation of "Standard Methods"-type treatability manuals. Such documents should incorporate the ideas and approaches of qualified specialists and be published through sponsoring organizations such as the American Petroleum Institute or the American Association of Professors in Sanitary Engineering.

10. The necessary survey and treatability information should be available before any industrial treatment facility is designed. In order to be reasonably certain that the pollution control system envisioned will satisfy the requirements of the industry and regulatory authority, it is necessary that a comprehensive survey and treatability program be required. This requirement can be satisfied through the proper establishment of guidelines by the regulatory agency and/or industry management.

11. Wastewater surveys and treatability studies should reflect the possible influence of shift changes, week-end operations, seasonal variations, etc., on the wastewater characterization and its treatability. The more accurately these variations are documented in the preliminary phases, the greater the probability of of optimum plant design being achieved.

12. As many new instrumental approaches for analyzing wastewaters currently are being introduced, an evaluation of the instrument performance with respect to analytical efficiency, interferences, and general limitations should be documented by independent sources.

# INTRODUCTION

The purpose of this report is to compile and organize the many components which constitute a preliminary wastewater treatability study for the refinery and petrochemical industry. The preliminary investigation of petrochemical and refinery wastewaters and the factors essential for the development of design criteria for pollution abatement and control facilities are included.

Background information relative to present pollution control programs within the refining and petrochemical industry, including applicable treatment processes, current design practice, problem areas, and trends in pollution control programs within the industry are presented in the introductory chapter.

## SOURCES OF WASTEWATER

The sources of wastes emanating from refinery and petrochemical operations can be divided into five general categories (Rice, et al, 1969):

1. wastes containing a principal raw material or product resulting from the stripping of the product from solution;
2. by-products produced during reactions;
3. spills, slab washdowns, vessel cleanouts, sample point overflows, etc;
4. cooling tower and boiler blowdown, steam condensate, water-treatment wastes, and general washing water; and
5. storm waters, the degree of contamination depending on the nature of the drainage area.

The principal contaminants in the wastewaters include organics from residual products and by-products, oils, suspended solids, acidity, heavy metals and other toxic materials, color, and taste and odor-producing compounds. The concentration of $BOD_5$ and COD respectively in untreated refinery effluents has averaged 108 and 204 pounds per 1,000 bbl of crude oil refined (API,1960; Forbes and Witt,1965; Huber, 1967; Weston and Hart,1941). The pH of refinery wastewaters is normally alkaline, but may vary considerably depending on disposal of spent acids, acid washes, etc.

The large variety of compounds produced within the petrochemical and refinery industries makes the task of treating wastewaters difficult and complex. Wastewaters from plants manufacturing similar or even the same compounds usually display dissimilar characteristics. This can be ascribed to the use of different manufacturing processes coupled with the fact that the by-product disposal pattern may occur in a number of different ways. Hence, a wastewater treatability study should be undertaken when the treatment of petrochemical and refining wastes is considered.

## WASTEWATER TREATMENT METHODS

A detailed treatability evaluation of each waste stream is a prerequisite to determining the proper integration of unit processes which constitute an optimum waste treatment system. The waste treatment methods applicable to the refining and petrochemical industries can be categorized as follows: physical, chemical, biological, special in-plant methods, and ultimate disposal (The Cost of Clean Water,1967).

Physical methods include gravity separation, air flotation, filtration, centrifugation, vacuum filtration, evaporation, and carbon adsorption. Gravity separators and air flotation units, which are used extensively throughout the industry, are designed primarily for removal of free-floating oil and settleable solids. Filtration is used primarily as a pretreatment for deep well injection; and centrifugation and vacuum filtration are used for sludge dewatering. Evaporation ponds are often efficient, but are limited to areas where land is available and climatic conditions are favorable. Carbon adsorption is used to remove refractory organic substances.

Chemical treatment methods include coagulation-precipitation, chemical oxidation, ion exchange, and chemical pretreatment or sludge conditioning. These methods enhance oil and solids removal, particularly with respect to oil emulsions.

The biological treatment methods include activated sludge and its modifications, trickling filters, aerated lagoons, and waste stabilization ponds. Usually some form of wastewater pretreatment is required to remove oils, suspended solids, and toxic substances, and to provide neutralization, equalization, and surge or holding capacity. The activated sludge process is generally considered the most effective biological process for removing organic materials with removal efficiencies in the range of 70 to 95 percent for $BOD_5$, 30 to 70 percent for COD, and 65 to 99 percent for phenols and cyanides (The Cost of Clean Water,1967). The conventional activated sludge process is the most widely applied. Contact stabilization is most applicable when a large fraction of the organic constituents is in suspended or colloidal form. Extended aeration is particularly adaptable to industrial applications as the longer detention periods allow the microorganisms more time to degrade the complex organics and, more importantly, sludge production is minimized.

Deep well injection of petrochemical and refinery wastewaters is used primarily as an ultimate disposal method for low-flow, highly concentrated wastes. The efficacy of disposing of these streams by deep well injection depends on the extent of pre-injection treatment requirements, the receiving formation, and the risks involved in contaminating overlying or underlying aquifers.

The more important in-plant treatment control methods include stripping and recovery operations, neutralization and oxidation of spent caustics, ballast water treatment, slop oil recovery, and temperature control. The practice of such in-plant treatment methods not only reduces the waste loadings to the treatment facility, but also enhances its performance. In some cases, in-plant control will show a cost credit in the form of product recovery.

An integral part of in-plant treatment procedures is adequate in-plant waste control practices. In-plant control techniques include salvage of unreacted chemicals, recovery of by-products, multiple reuse of water, good housekeeping techniques to reduce leaks and spills, and curbing and diking of drainage areas. These controls can reduce both the volume and concentration of pollutants requiring treatment.

New production methods are being directed toward increases in product yield, often resulting in reduced amounts of by-products and unused raw materials in waste streams. A more general indication of pollution reduction by in-plant processing practices is the much lower pollutant loadings per unit of throughput for "newer" refineries as compared to "older" refineries (The Cost of Clean Water, 1967).

## CURRENT DESIGN PRACTICE

To date, biological treatment methods have afforded the most economical secondary treatment processes for pollution abatement. In order to minimize biological treatment costs, several pretreatment processes have been adopted, depending on the characteristics of the waste streams being treated. Design of biological treatment units must consider the possibility of spills, storm runoff, ballast water handling, variation in flow and contaminants, and toxic or inhibitory substances. Completely mixed activated sludge units, therefore, are applicable to dampen these fluctuations and inhibitory effects. Aerated lagoons are often used where the waste has a large volume but relatively low concentration of dissolved organics. Anaerobic lagoons, anaerobic contact units and high rate trickling filters are used individually or conjunctively when high strength wastes are involved.

Facilities for handling the treatment of the accumulated primary and biologically synthesized sludges often represent a major portion of the treatment facility costs. One inexpensive method of disposing of sludges practiced in many parts of the country is lagooning. However, dewatering the sludge to reduce the volume or direct disposal at sea or in remote areas may be more favorable alternatives where land is unavailable. Aerobic digestion is presently favored over anaerobic treatment in industrial waste applications and is generally followed by thickening, vacuum filtration, filter pressing, or centrifugation and ultimate disposal by incineration or trucking.

## PROBLEM AREAS

The problem areas encountered in the treatment of wastes discharged from the refining and petrochemical industries are generally those associated with pretreatment and biological treatment systems. Problems may be attributed to process changes or modifications, accidental spills resulting in the discharge of slugs of contaminants, or poor in-plant management.

Problems related to pretreatment processes may be caused by excess concentrations of free and emulsified oils, high or widely fluctuating temperatures, acidity or alkalinity, or other contaminants which adversely affect process operation.

Waste oil usually occurs from leaks, spills, washing operations, and rainfall runoff from oily areas. When oily wastes and water commingle, there is always a good chance for emulsification, which sometimes is difficult and costly to break.

Wastes affecting pH in the refinery and petrochemical industries include strong acids and alkalies as well as dissolved solids which often buffer their effects. Spills, leaks, scrubbing operations, and point discharges of spent acid are the main sources of acid wastes while the main contributor of acidity is sulfuric acid. However, HCl, $H_2S$, HF, and $CO_2$ contribute to a lesser extent to the acidity of the wastewater. Alkalies from process neutralization, process operations, and kettle washes are the main sources of alkalinity.

The oxygen demand of refinery and chemical wastewaters is probably the most important factor to be considered. The most concentrated oxygen-demanding wastes discharged from a refinery usually occur in the crude and cracking units. Although much of this oxygen demand in terms of BOD, TOC, COD, etc. is attributable to the oily fraction, a significant portion results from the presence of lighter hydrocarbon contaminants. Moreover, substances such as sulfides and various nitrogen compounds are responsible for an additional oxygen demand.

Toxicity to living organisms is a critical factor in evaluating the treatability of chemical and refinery wastes. Ammonium salts, sulfides and polysulfides resulting as wastes from the use of ammonia as an anticorrosive agent, as well as other boiler and cooling tower inhibitors are toxic. Heavy metals used as catalysts or preparants in process operations are other sources of pollutants which may be toxic to living organisms.

The taste and odor-producing wastes resulting from washing high sulfur crude oil, or cracked distillate from high sulfur stocks, may have highly noticeable and persistent odors. The odor is attributable to complex organic sulfur compounds and alkylated substances.

Acid sludges are the next most important group responsible for taste and odor problems. Sludges from the acid treatment of light distillates have a much more pronounced odor than those from the treatment of lubricating stocks. Much of the odor from light oil sludges is due to mercaptans, which are disagreeable and can be detected at concentrations of a fraction of a part per trillion.

Large concentrations of sulfides in biological treatment units impair the treatment efficiency of these units because of the oxygen required to satisfy the chemical oxygen demand or the possible inhibitory or toxicological effects on the system bacteria. Preaeration of sulfide wastes results in stripping the sulfide from solution when the wastewater is acidic, or oxidizing the sulfides to thiosulfate or sulfate at high pH values.

## SOLID WASTE DISPOSAL METHODS

A historical survey of the trends in solids disposal at refineries and petrochemical plants indicated that this is a significant problem with most industries. Landfill was found to be the most common method of disposal and was used primarily for separator and tank bottom sludges, sewer cleanings, water treating sludges, cooling tower bottoms, and biological treatment plant sludges. Incineration and open burning has been used for general refuse. Contract disposal services have been used for filter cakes, treating clays, and slop oil disposal.

Based on the results of this survey, it was decided that further information on the following areas would improve the disposal techniques available:

1. determination of hydrocarbon content and calorific values of solid wastes,

2. evaluation of incinerators to establish capabilities for handling different wastes,

3. investigation of land spreading techniques to establish land and manpower requirements,

4. identification of wastes that are amenable to de-oiling treatment, i.e., separation of solids and hydrocarbons, and

5. investigation and development of spent caustic disposal systems.

## RECOMMENDED APPROACH FOR SUCCESSFUL POLLUTION ABATEMENT PROGRAMS

The successful result of a pollution abatement program depends on a number of carefully integrated procedures designed in cooperation with and dependent upon each other. These procedures are divided into 6 steps illustrated in Figure 1. Consideration of the sources and quantity of pollutants should be made during the research and design phase of an industrial plant and this should be performed prior to the construction of new facilities or additions. One procedure which has been applied to refineries in the design and planning stages is to estimate the mass balance around each unit processes as well as process areas (Sun Oil Company, 1969). Alteration of the design of various units to minimize wastewater flows and the incorporation of new and more efficient processes are the most obvious means of reducing a source of pollution. The objective of the wastewater survey is to determine all sources of wastewaters and obtain representative samples of those available. The future sources and potential problems should also be considered during the survey.

While no one unit process can effectively treat refinery and petrochemical wastewaters, there are combinations of biological, chemical, and physical processes which can be used to stabilize the wastewaters. Although these wastewaters often have biological inhibitors, recent studies have shown that the activated sludge process (Engineering-Science, Inc./Texas, Delaware Study; Kerberger and Barnhart, 1970) and algal stabilization ponds (Copeland and Dorris, 1964; Copeland, Minter and Dorris, 1964) are relatively unaffected by various refinery wastewaters provided the proper safequards are designed into the facility.

When secondary and tertiary treatment are necessary, the ultimate step of closing the water-wastewater loop becomes a valid consideration. The economics of closed-loops within an industry or within a municipality have already been realized in many cases (Partridge and Paulson, 1967; Cecil, 1969).

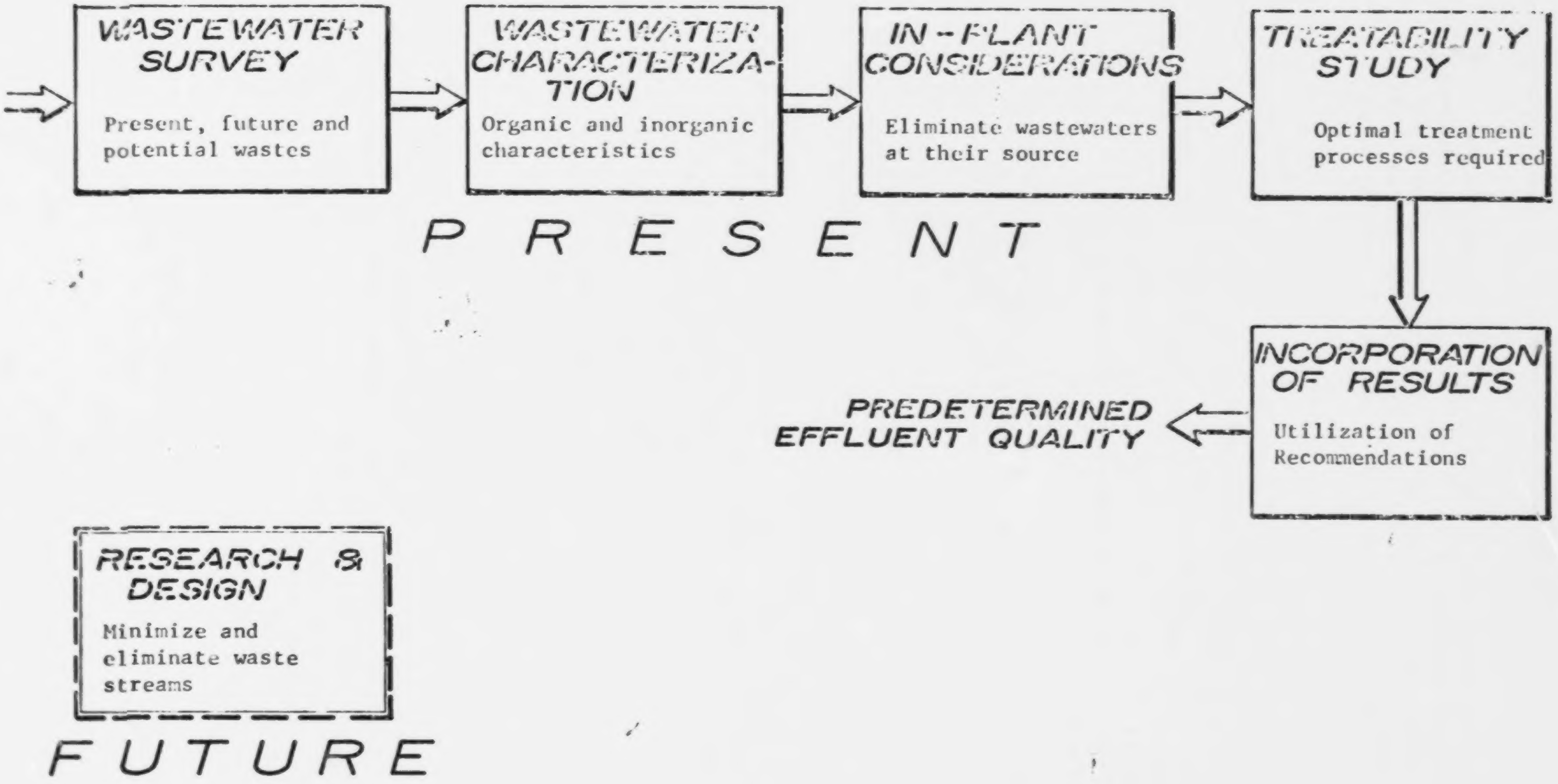

WASTEWATER SURVEY
Present, future and potential wastes
WASTEWATER CHARACTERIZATION
Organic and inorganic characteristics
IN-PLANT CONSIDERATIONS
Eliminate wastewaters at their source
TREATABILITY STUDY
Optimal treatment processes required
PRESENT
INCORPORATION OF RESULTS
Utilization of Recommendations
PREDETERMINED EFFLUENT QUALITY
RESEARCH & DESIGN
Minimize and eliminate waste streams
FUTURE

FIGURE 1
SEQUENTIAL STEPS REQUIRED TO MINIMIZE AND ELIMINATE THE POLLUTIONAL EFFECT OF WASTEWATERS FROM REFINERY AND PETROCHEMICAL INDUSTRIES.

## THE WASTEWATER SURVEY

The wastewater survey must contain detailed information on waste flows, characteristics of the flows, and relevant environmental conditions in order that sound engineering decisions regarding the wastewater treatment can be made. Design data for wastewater treatment facilities should include but not be limited to the following:

1. the source of all significant waste streams;
2. samples at points where significant changes in waste characteristics or quantity of flow occur;
3. samples which reflect the benefits from segregated sewer systems;
4. consideration of water reuse and water saving process modifications;
5. consideration of overloading of waste treatment systems resulting from unit shutdown, startups, turn-arounds, accidental dumping or spills, and other shock loadings;
6. investigation of reducing waste streams by eliminating or decreasing flows by process modifications; and
7. evaluation of wastewater sources related to variable occurrences such as storm flow drainage.

A complete audit of all water and contaminants entering and leaving a process or drainage area would yield sufficient information to satisfy the objectives of a wastewater survey. Practically, however, this mass balance is seldom possible to achieve due to unexpected and unknown variations in raw materials, chemical inputs, process operations, etc. Constraints placed on the industry such as required quality standards, limited financial resources, and pollution abatement policies often dictate the scope of a wastewater survey. This chapter presents a practical engineering approach to obtaining the necessary information.

### SAMPLING STATION SELECTION

Petrochemical and refinery liquid wastes may be classified as clean or highly contaminated process streams, clean and contaminated storm systems, and sanitary waste streams. The selection of wastewater sampling sites should be based on obtaining characterization data for each of the applicable categories, since segregation of wastewater conveyance systems gives more flexibility in solving pollution control problems.

A number of sources of clean, oily, and sanitary refinery wastewaters are identified in Figure 2 and the more common sources of highly contaminated wastewaters are summarized in Figure 3. In any wastewater survey it may be necessary to determine the capacity and effectiveness of existing in-plant processes such as those shown in these Figures.

"Clean" process streams normally are those discharged from cooling and boiler utility areas and from general washing operations. Under most operating conditions, 85 to 95 percent of the water used in petroleum refineries is for cooling purposes (API, 1968). In "once-through systems" the major change in water quality will be only an increase in temperature. Recycled cooling water may have high salt concentrations due to evaporation loses as well as high concentrations of chromate or other toxic materials added for prevention of corrosion and/or growth of microorganisms. Other streams with relatively high concentrations of dissolved solids, i.e., boiler blowdown, neutralized demineralized resin rinses, etc., can be included. However, streams that may become contaminated with oil should be excluded. Thus, although organic contamination of these waters is usually not a problem, thermal considerations and the total dissolved solids concentration warrant careful attention.

Highly contaminated process streams include those streams containing concentrated organic materials, high concentrations of toxic substances, significant concentrations of oxygen-utilizing material (chemically and biologically oxidizable), extremely acidic and alkaline wastes, and oily streams containing high dissolved solids. These wastes usually originate from process operations, cleaning and washing, or accidental leaks or spills. Process discharges are caused by reaction products created by impurities in the feedstock, raw or partially reacted feed chemicals resulting from low process conversion efficiencies, and by-product formation in the chemical reactor.

Acidic wastes are among the most important wastes of petroleum refineries and originate principally in the treating plants, acid recovery areas, alkylation units, some water treating plants, and in some special product operations. They result from washing of intermediate petroleum products which have been acid treated, and from leakage and spills around these process areas and the leaching of acid wastes by rainwater.

Excessive alkalinity is normally not a problem although waste caustic or caustic sludges often merit special consideration. It varies in composition and appearance, depending on the crude being processed or the oils being washed. Waste causticity resulting from washing crudes and mixed paraffinic and naphthenic substances contain about 0.3 percent unreacted caustic soda, sodium sulfide, sulfate, sulfite, thiosulfate, phenol, mercaptans, and other organics.

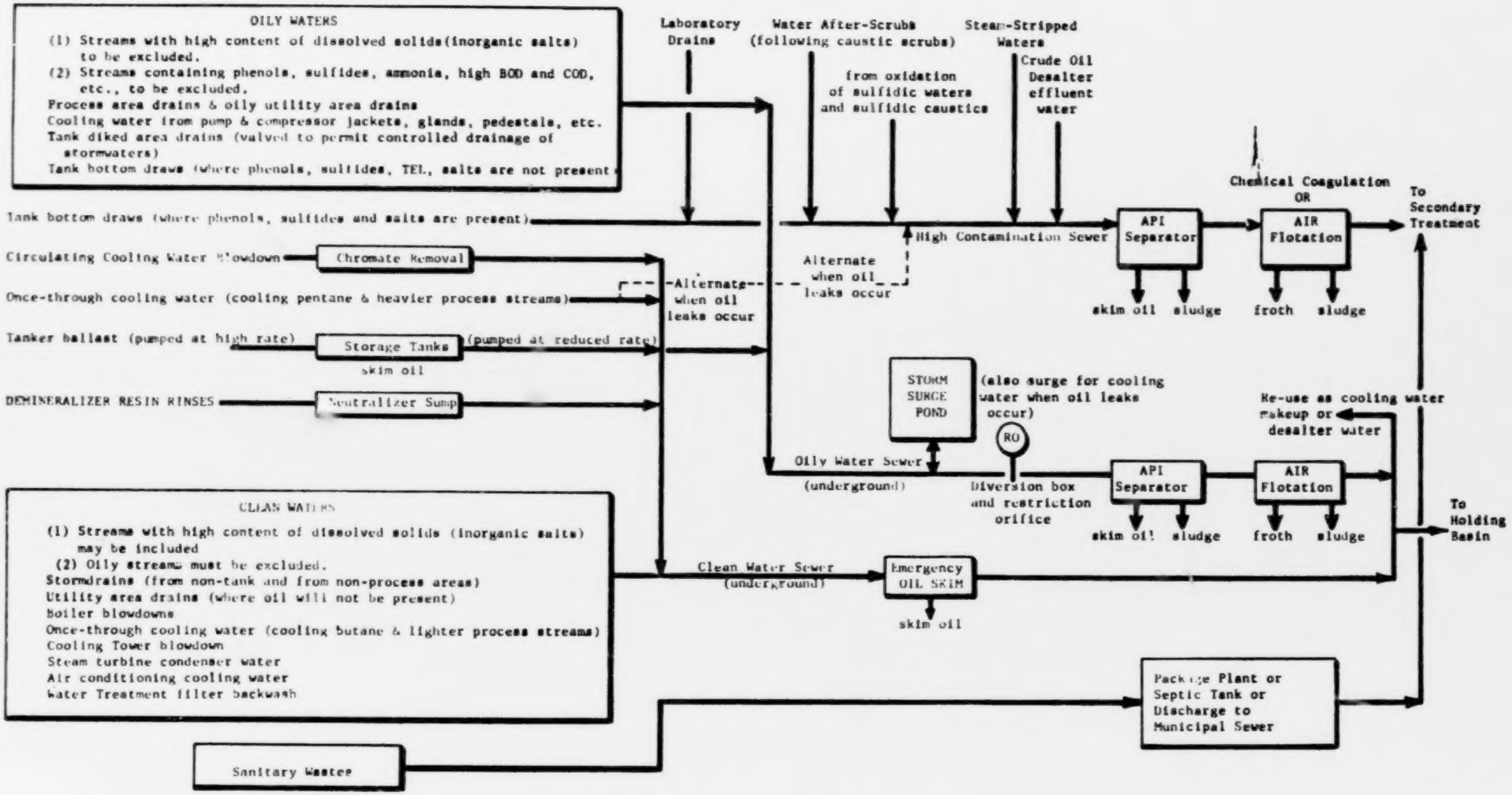
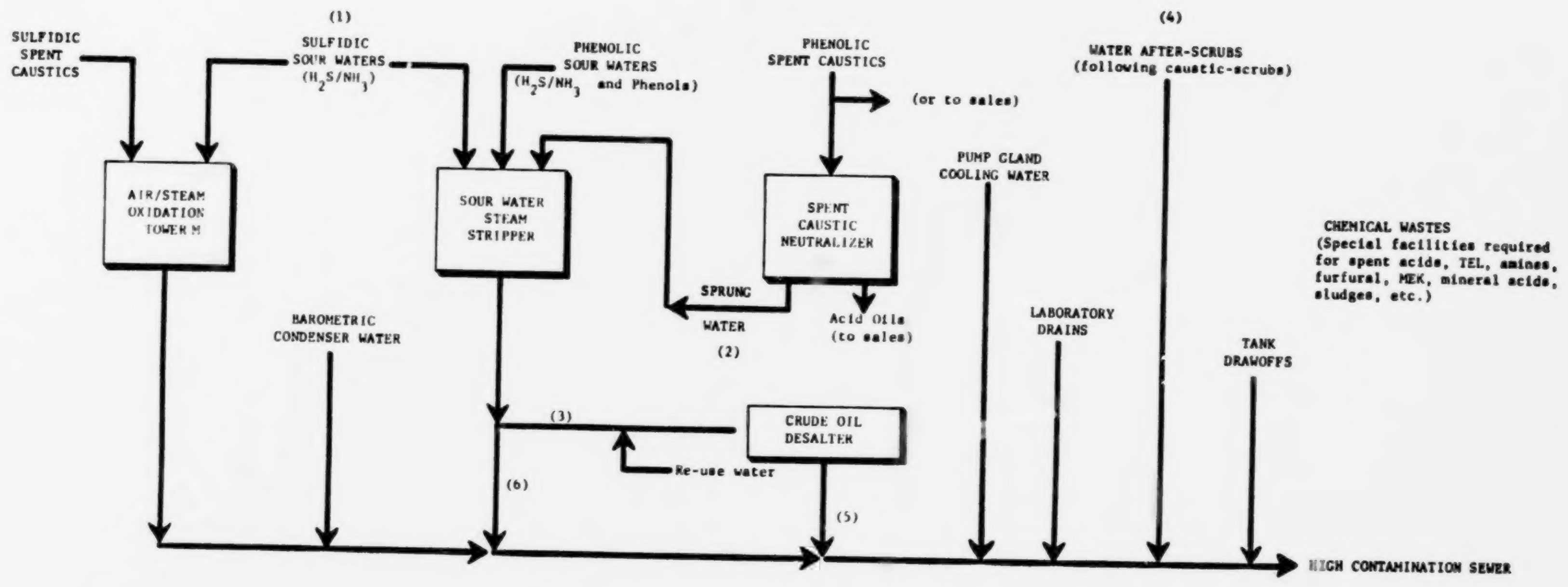

OILY WATERS
(1) Streams with high content of dissolved solids (inorganic salts) to be excluded.
(2) Streams containing phenols, sulfides, ammonia, high BOD and COD, etc., to be excluded.
Process area drains & oily utility area drains
Cooling water from pump & compressor jackets, glands, pedestals, etc.
Tank diked area drains (valved to permit controlled drainage of stormwaters)
Tank bottom draws (where phenols, sulfides, TEL, salts are not present)
Laboratory Drains
Water After-Scrubs (following caustic scrubs)
from oxidation of sulfidic waters and sulfidic caustics
Steam-Stripped Waters
Crude Oil Desalter effluent water
Chemical Coagulation OR
Tank bottom draws (where phenols, sulfides and salts are present)
High Contamination Sewer
API Separator
AIR Flotation
To Secondary Treatment
skim oil
sludge
froth
sludge
Circulating Cooling Water Blowdown
Chromate Removal
Once-through cooling water (cooling pentane & heavier process streams)
Alternate when oil leaks occur
Alternate when oil leaks occur
Tanker ballast (pumped at high rate)
Storage Tanks
(pumped at reduced rate)
skim oil
DEMINERALIZER RESIN RINSES
Neutralizer Sump
STORM SURGE POND
(also surge for cooling water when oil leaks occur)
RO
Re-use as cooling water makeup or desalter water
Oily Water Sewer
(underground)
Diversion box and restriction orifice
API Separator
AIR Flotation
skim oil
sludge
froth
sludge
To Holding Basin
CLEAN WATERS
(1) Streams with high content of dissolved solids (inorganic salts) may be included
(2) Oily streams must be excluded.
Stormdrains (from non-tank and from non-process areas)
Utility area drains (where oil will not be present)
Boiler blowdowns
Once-through cooling water (cooling butane & lighter process streams)
Cooling Tower blowdown
Steam turbine condenser water
Air conditioning cooling water
Water Treatment filter backwash
Clean Water Sewer (underground)
Emergency OIL SKIM
skim oil
Package Plant or Septic Tank or Discharge to Municipal Sewer
Sanitary Wastes

FIGURE 2

SEWER SEGREGATION AND OIL REMOVAL


SULFIDIC SPENT CAUSTICS
(1)
SULFIDIC SOUR WATERS ($H_2S/NH_3$)
PHENOLIC SOUR WATERS ($H_2S/NH_3$ and Phenols)
PHENOLIC SPENT CAUSTICS
(or to sales)
(4)
WATER AFTER-SCRUBS (following caustic-scrubs)
AIR/STEAM OXIDATION TOWER M
SOUR WATER STEAM STRIPPER
SPENT CAUSTIC NEUTRALIZER
PUMP GLAND COOLING WATER
CHEMICAL WASTES (Special facilities required for spent acids, TEL, amines, furfural, MEK, mineral acids, sludges, etc.)
SPRUNG WATER
(2)
Acid Oils (to sales)
BAROMETRIC CONDENSER WATER
LABORATORY DRAINS
TANK DRAWOFFS
(3)
CRUDE OIL DESALTER
Re-use water
(6)
(5)
HIGH CONTAMINATION SEWER

(1) Usually steam stripped, if no phenols or oil present, may be oxidized.

(2) Will contain about 3000 ppm wt. $H_2S$, 8000 ppm wt. phenols, and 15-30 wt.% sodium salts. High salt content may cause problems in steam stripper.

(3) Stripper removes about 98% of $H_2S$, 95% of $NH_3$ and 20% of phenols, pH of stripped water will be about 9-10. With some crudes, residual $NH_3$ may require acid neutralization of pH 6.8-7.0 to avoid formation of soaps in desalter.

(4) May require acid neutralization if caustic carryover is excessive.

(5) Desalter removes most of the phenols and $H_2S$ from water. This stream will contain 0-10 ppm wt. $H_2S$, 10-25 ppm wt. phenols, 100-300 ppm wt. oil, 50-500 ppm wt. BOD.

(6) $H_2S$ content about 10-150 ppm wt. and $NH_3$ content about 50-500 ppm wt. pH about 9-10. Will also contain phenols.

FIGURE 3

IN-PLANT PRETREATMENT OF HIGH CONTAMINATION WASTE STREAMS

Contaminated sewers usually contain "oily" wastewaters, although parallel sewers are provided occasionally to separately convey oily concentrated and non-oily concentrated waste streams. Oily sewers are routed to oil separation and recovery processes such as API gravity separators and air flotation units. This not only reduces the oil concentration of the unit process underflow flowing to subsequent treatment facilities, but also provides for oil recovery through skimming, emulsion breaking, storage, and reprocessing of recovered oil.

Sanitary waste streams emanating from administrative and laboratory areas are usually separated from industrial source discharges in order to prevent chlorinating the total combined flow. Consequently, these streams are usually separated from the industrial flow and treated separately.

## CASE STUDIES OF WASTEWATER SURVEYS

The following wastewater surveys are presented as case histories to document typical wastewater surveys. Although the goals and objectives of the studies cited were different, they represent typical approaches utilized in conducting surveys to fulfill predetermined objectives.

### Case History A - Petrochemical Industry

This survey was conducted in a large petrochemical complex having a total water use of 2.5 MGD. The primary products include butadiene, olefins, styrene, and nylon monomers.

At the time of the survey, the waste treatment system consisted of various in-plant recovery devices, oil separation facilities, neutralization systems, and deep injection wells with appropriate surface pretreatment units.

The objectives of the survey were as follows:

1. locate and classify major sources of pollution, organic and inorganic;
2. categorize the major sub-collection systems as to their amenability to biological treatment, and
3. identify waste discharges with
    a. high toxicity potential on the proposed treatment system and receiving environment, and
    b. product recovery potential.

In order to fulfill these objectives, a comprehensive wastewater survey leading to the characterization and categorization of major waste streams was undertaken. Sampling points were selected in order to evaluate major sources of pollution. These sites are graphically illustrated in Figure 4 and are tabulated in Table 1.

After checking plant operational schedules and programming, it was determined that a 24-hour survey would indicate typical flows and characteristics, providing the sampling was sufficiently frequent and proper techniques of acquiring and compositing the sample were employed.

The flows of each of the major collection systems were estimated by measuring the depth and velocity of the partially filled gravity sewers, using the recorded slopes from construction drawings for verification. In some instances, the total flow from various locations within the complex was pumped and the flow charts were used as the basis of estimating flow. Grab samples were taken at each sampling station during the 24-hour period and composited according to flow at 2-hour intervals. These composited samples were then cooled to 4°C and stored until the survey had been completed. All samples were then collected and transported to the laboratory for chemical analysis. The analyses selected for this particular survey are itemized in Table 2.

Once the analyses had been performed, the statistical distribution of the data was obtained and used in formulating design criteria. For example, the degree of variation was particularly significant when considering average values for design parameters. Additionally, the variation was descriptive of the nature of production process operations which is important when conceiving treatment system layout, in-plant modifications, or factors of safety to be incorporated into the sizing of the system.

The general conclusions resulting from this survey of the petrochemical plant as described herein can be summarized as follows.

1. The wastewater from network "A" was found to have a low volume of flow, although high concentrations and variability of dissolved organic and inorganic constituents were observed.

2. The network "A" stream analysis indicated the presence of some product spills and generally poor in-plant housekeeping. Concurrently, product recovery potential was indicated and steps were recommended to minimize this waste stream.

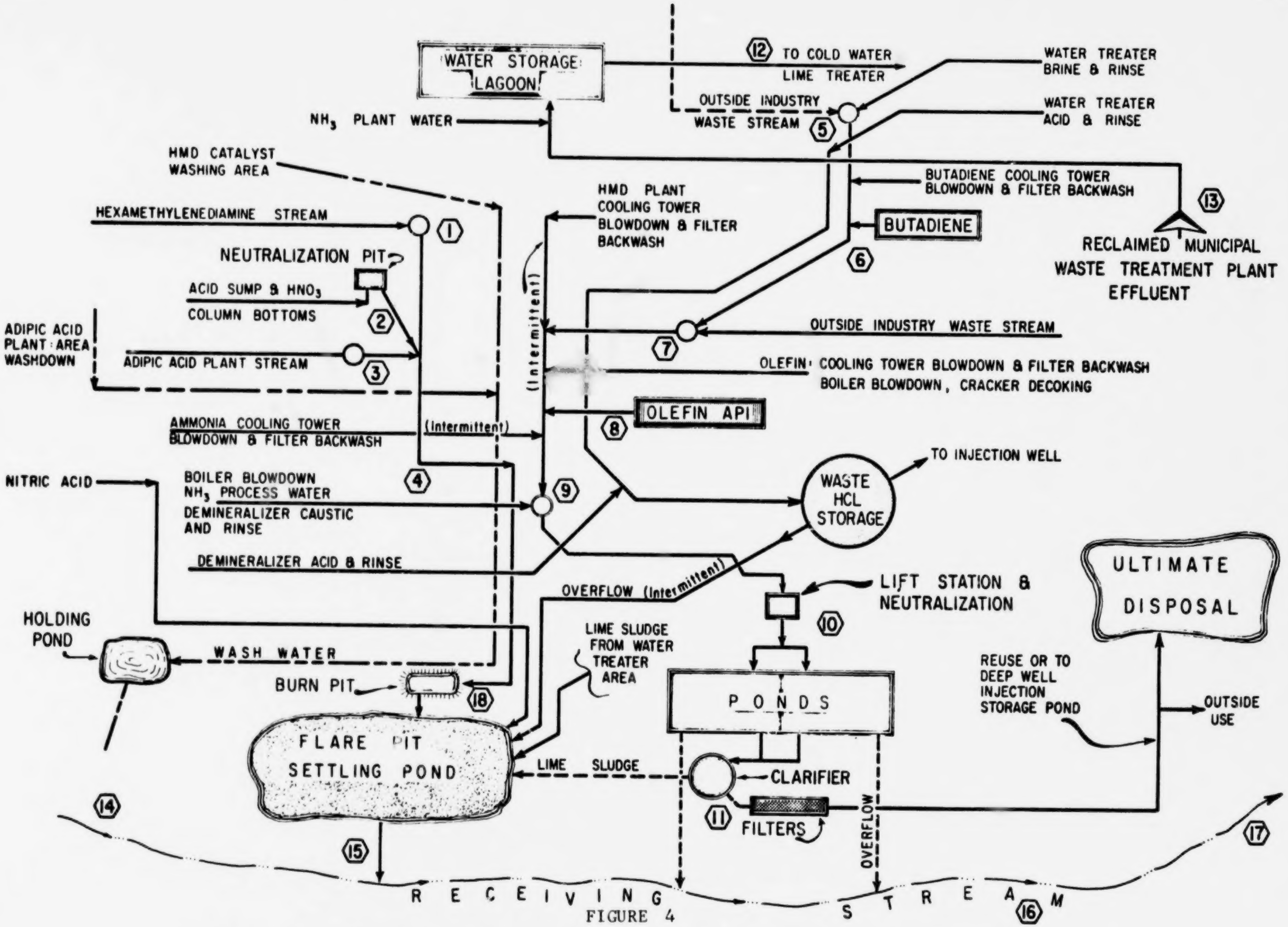

WATER STORAGE LAGOON
⑫ TO COLD WATER LIME TREATER
WATER TREATER BRINE & RINSE
WATER TREATER ACID & RINSE
OUTSIDE INDUSTRY WASTE STREAM ⑤
NH$_3$ PLANT WATER
HMD CATALYST WASHING AREA
BUTADIENE COOLING TOWER BLOWDOWN & FILTER BACKWASH
⑬
HMD PLANT COOLING TOWER BLOWDOWN & FILTER BACKWASH
BUTADIENE
⑥
RECLAIMED MUNICIPAL WASTE TREATMENT PLANT EFFLUENT
HEXAMETHYLENEDIAMINE STREAM ①
NEUTRALIZATION PIT
ACID SUMP & HNO$_3$
COLUMN BOTTOMS
②
ADIPIC ACID PLANT AREA WASHDOWN
ADIPIC ACID PLANT STREAM ③
(Intermittent)
OUTSIDE INDUSTRY WASTE STREAM
⑦
OLEFIN COOLING TOWER BLOWDOWN & FILTER BACKWASH
BOILER BLOWDOWN, CRACKER DECOKING
AMMONIA COOLING TOWER BLOWDOWN & FILTER BACKWASH
(Intermittent)
⑧ OLEFIN API
④
TO INJECTION WELL
NITRIC ACID
BOILER BLOWDOWN
NH$_3$ PROCESS WATER
DEMINERALIZER CAUSTIC AND RINSE
⑨
WASTE HCL STORAGE
DEMINERALIZER ACID & RINSE
OVERFLOW (Intermittent)
LIFT STATION & NEUTRALIZATION
⑩
ULTIMATE DISPOSAL
HOLDING POND
WASH WATER
LIME SLUDGE FROM WATER TREATER AREA
BURN PIT
⑱
PONDS
REUSE OR TO DEEP WELL INJECTION STORAGE POND
OUTSIDE USE
FLARE PIT SETTLING POND
LIME SLUDGE
CLARIFIER
⑭
⑪
FILTERS
OVERFLOW
⑮
⑰
RECEIVING STREAM
⑯

FIGURE 4

EXAMPLE OF WASTEWATER SAMPLING STATION LOCATION IN A COMPLEX PETROCHEMICAL INDUSTRY

TABLE 1

## SAMPLING STATION DESCRIPTION

| Sampling Point Designation | Description |
|---|---|
| NETWORK "A" | |
| 1 | Hexamethylene diamine area |
| 2 | Acid sump and column bottoms (neutralization) |
| 3 | Adipic acid production area |
| 4 | Total network "A" flow (API Separator effluent) |
| NETWORK "B" (Butadiene, Olefin Production Area, Outside Industry Stream, Blowdown Cooling Stream, Miscellaneous Streams) | |
| 5 | Outside industry waste stream |
| 6 | Butadiene production area (API Separator effluent) |
| 7 | Outside industry waste stream (manhole) |
| 8 | Olefin production area (API Separator effluent) |
| 9 | Four through Seven flow plus blowdown, ammonia process water |
| 10 | Total flow |
| 11 | Total flow |
| NETWORK "C" (Treated Sewage Effluent) | |
| 12 | Treated sewage effluent (sampling port) |
| 13 | Municipal treatment plant effluent |
| 14 | Catalyst washing area, surface runoff (open ditch) |

## TABLE 1 (Cont)

## SAMPLING STATION DESCRIPTION

| Sampling Point Designation | Description |
|---|---|
| NETWORK "C" (Cont) | |
| 15 | Flare pit settling pond overflow |
| 16 | Upstream receiving water |
| 17 | Downstream receiving water |
| 18 | Nitric acid stream (sampled at Flare Pit Settling Pond) |

TABLE 2

## ANALYSES COMPLETED IN A WASTEWATER CHARACTERIZATION STUDY OF A PETROCHEMICAL INDUSTRY

| Sampling Point | Analyses Performed | Purpose |
|---|---|---|
| NETWORK "A", "B", and "C" | TOC<br>COD | Degree of organic treatment required |
| | pH, alkalinity, acidity | Neutralization requirements |
| | Total Solids | |
| | Suspended | Pretreatment requirements |
| | Dissolved | Effect on treatment process; estimate of effluent quality with respect to that allowable |
| | Total Kjeldahl Nitrogen | Nutrients |
| | Total Phosphate | Nutrients |
| | Sulfates | Effect on proposed treatment process; effluent quality requirements |
| | Chlorides | Effect on proposed treatment processes; effluent quality requirements |
| | Oils | Efficiency of existing oil recovery systems; effect on proposed treatment processes; effluent quality requirements |
| | Temperature | Thermal pollution potential; basis for calculating temperature balances and effect on temperature dependent reactions |

3. Preliminary observations of the network "A" stream indicated difficulty in applying biological treatment methods for this source individually, without dilution water from other sources.

4. The network "B" stream had a much higher volume of flow with much lower concentrations of organic and inorganic contaminants. The variation of these materials was also less. However, the suspended solids load from processes served in this network was higher.

5. The network "B" stream appeared to be more amenable to conventional treatment applications than did the network "A" stream, although a preliminary step for removal of suspended solids would be required prior to subsequent secondary forms of treatment.

## Case History B - Refinery-Petrochemical Complex

The objectives of this survey were different than the one previously cited in that the effects of the combined flow on an operating aerated lagoon and its performance characteristics were to be evaluated.

Generally, the wastewaters included those from refinery process operations, cooling and boiler units, and miscellaneous cleaning and washdown operations. Some forms of pretreatment were given to most streams within the complex. For example, most oily streams such as those emanating from ballast dumps or in-plant separations were routed through a series of oil separation units prior to being pumped into the aerated lagoon.

It was determined that a 24-hour sampling and analysis period was sufficient to accurately characterize the performance of the lagoon. The approach in making this evaluation was to measure the level of organic and inorganic constituents for the influent and effluent, thus measuring organic removal efficiency as well as conversion levels of inorganic substances. Concurrently, representative sampling profiles were established within the aerated lagoon basin in order to establish mixing and dispersion patterns necessary for the proper placement of mechanical surface aerators. The sampling and analysis schedules for the survey are itemized in Tables 3 and 4.

The general conclusions drawn from this aerated lagoon survey are listed as follows:

1. The efficiency of the aerated lagoon in terms of biological removal of soluble organic materials was approximately equal to that predicted in preliminary bench scale treatability studies.

## TABLE 3

## SAMPLING AND ANALYSIS SCHEDULE INFLUENT AND EFFLUENT STATIONS

| Analyses | Frequency | Purpose |
|---|---|---|
| BOD (five-day) (mg/l) | 1/hr | organic load, plant effluent with respect to criteria |
| BOD (ultimate) (mg/l) | 1/hr | organic load, plant effluent with respect to criteria |
| COD (mg/l) | 1/hr | organic BOD comparison |
| Conductivity (mhos/cm) | 1/hr | waste characterization |
| D. O. (mg/l) | continuous | process control |
| Flow (mgd) | continuous | organic and hydraulic load |
| Oils (mg/l) | 1/hr | process control, toxicity, efficiency of existing oil recovery systems |
| ORP (mv) | 1/hr | sulfide level; ratio of oxidants to reductants |
| pH | continuous | process control |
| $NH_4$ - N (mg/l) | 1/hr | nutrients, waste characterization, potential toxicity |
| SS (mg/l) | 1/hr | suspended solids loading |
| Sulfates (mg/l) | 1/hr | sulfide oxidation, wastewater characterization; effect on subsequent waste stabilization ponds |
| TDS (mg/l) | 2/hr | waste characterization |
| Temp ($^{o}C$) | 1/hr | environmental, effect on temperature dependent reactions |
| VSS (mg/l) | 1/hr | volatile solids loading |

## TABLE 4

## SAMPLING AND ANALYSIS SCHEDULE PROFILES WITHIN AERATED LAGOON BASIN

| Analysis | Sampling Points | | Purpose |
|---|---|---|---|
| | Horizontal | Vertical | |
| $BOD_5$ (mg/1) | Every 20 feet | 1/top<br>1/mid-depth<br>1/bottom | Mixing evaluation with respect to soluble organics |
| D. O. (mg/1) | " | " | $O_2$ profiles, anaerobic areas, zone of aerator influence evaluation |
| $O_2$ Uptake | One Per Profile | mid-depth | Evaluate $O_2$ demand of basin contents; aerator efficiency |
| ORP (mv) | " | " | Oxidant-reductant profile |
| TOC (mg/1) | " | " | Mixing evaluation with respect to soluble organics |
| TSS (mg/1) | " | " | Uniformity of TSS, effectiveness of aerators in maintaining solids in suspension |
| Velocity (fps) | " | " | Velocity profiles, mixing evaluation |

2. There was an accumulation of heavy oily sludge in the bottom of the lagoon, indicative of the relatively high oily solids loading applied directly to the lagoon as well as the inability of the surface aerators to keep this sludge in suspension at the power level employed.

3. The power level of 0.05 HP/1000 gallons of basin volume was insufficient to keep all of the biological solids in suspension and pronounced gradients of D.O., SS, and liquid velocities were noted in the lagoon. However, a small residual D.O. level was noted at most horizontal and vertical sampling stations within the aerated basin.

4. The rapid increase of D.O. in the aerated lagoon when the wastewater inflow was temporarily diverted and the equally rapid decrease when the flow was returned to the lagoon indicated that the microbial floc was viable and active.

## Case History C - Petrochemical Complex

A survey of this petrochemical facility producing polyester resins was conducted in order to determine the feasibility of treating the liquid wastes using biological methods. Although the plant produced a relatively low total waste flow in terms of volume, the wastewater organic concentration was highly fluctuative.

The sources of wastewater discharged from the facility were categorized as follows:

1. Process wash and rinse - this wastewater results from periodic cleaning of reaction vessels;

2. Base flow - a composite of wastewaters discharged from a multitude of sources exclusive of those derived from scrubber or process wash/rinse operations;

3. Storm runoff - the portion of storm drainage which comes in contact with contaminated areas; and,

4. Scrubber blowdown - from intermediate product washes.

The average COD and pH of these four waste streams are given in Table 5. The final recommendations of this survey included:

1. segregation of the highly concentrated scrubber blowdown from the remaining waste streams using liquid incineration as the disposal process; and,

2. altering the collection system for the remaining waste streams, including storm water, to be discharged to a single point and treating this flow biologically.

## TABLE 5

## WASTEWATER CHARACTERISTICS FROM A SMALL PETROCHEMICAL INDUSTRY

| Description of Waste Source | COD (mg/1) | pH |
|---|---|---|
| Intermittent Washing Operations | 6,000 | variable* |
| Base Flow From Process Operations | 2,500 | 8.0 |
| Storm Runoff (Design Basis = Two-Year Storm) | 2,000 | --- |
| Off-gas Scrubber Blowdown | 100,000 | 1.5 |

* Depends on Whether Process Wash or Process Rinse is being discharged.

This concept was complicated to some extent because of the discontinuous pattern of flow. However, the impact of variable loading was sequestered by providing a completely mixed biological treatment basin sized for excess capacity. The results of continuous monitoring of all wastewater from this industry prior to in-plant segregation and equalization is shown in Figure 5 while the effect of in-plant changes and equalization is shown in Figure 6.

### Case History D - Petrochemical Complex

This survey is cited to document the significance of storm runoff as a source of pollution. Rainfall information for this small petrochemical complex producing polyester resins was obtained from the Weather Bureau and the calculated volume of runoff for several 24-hour design storms is given in Table 6. A runoff coefficient of 0.90 was used to estimate these volumes accumulating from the 13 acre contaminated area of the plant. Samples of runoff were taken during storm conditions and COD values up to 2500 mg/l were reported during the peak portion of the flow. Recommendations were made to provide retention facilities to store the first 15 minutes of runoff resulting from a 5-year storm, then discharging this contaminated volume of water to the biological facility over an extended period of time. It is impractical in most cases to provide retention ponds when production and storage facilities encompass large areas. The calculated storage required to retain the contaminated fraction of a 5-year storm from one refinery complex occupying several thousand acres, for example, is 235,000,000 gallons (Engineering-Science, 1969).

### Case History E - Chemical Complex

Storm runoff presented a different problem for a reprocessing chemical facility as shown in Figure 7(Gloyna, Ford and Eller, 1969). Samples were collected at the storm collection sump for each of the 6 contaminated areas. The varying magnitudes and patterns of runoff COD enabled the engineers to make decisions for collecting, storing and reprocessing the concentrated portion of the storm flow while using the less concentrated waters for boiler and cooling tower make-up. This approach not only provided credits in terms of recovering product and reducing fresh water make-up requirements, but also reduced the volume of contaminated storm runoff leaving the property of the chemical plant.

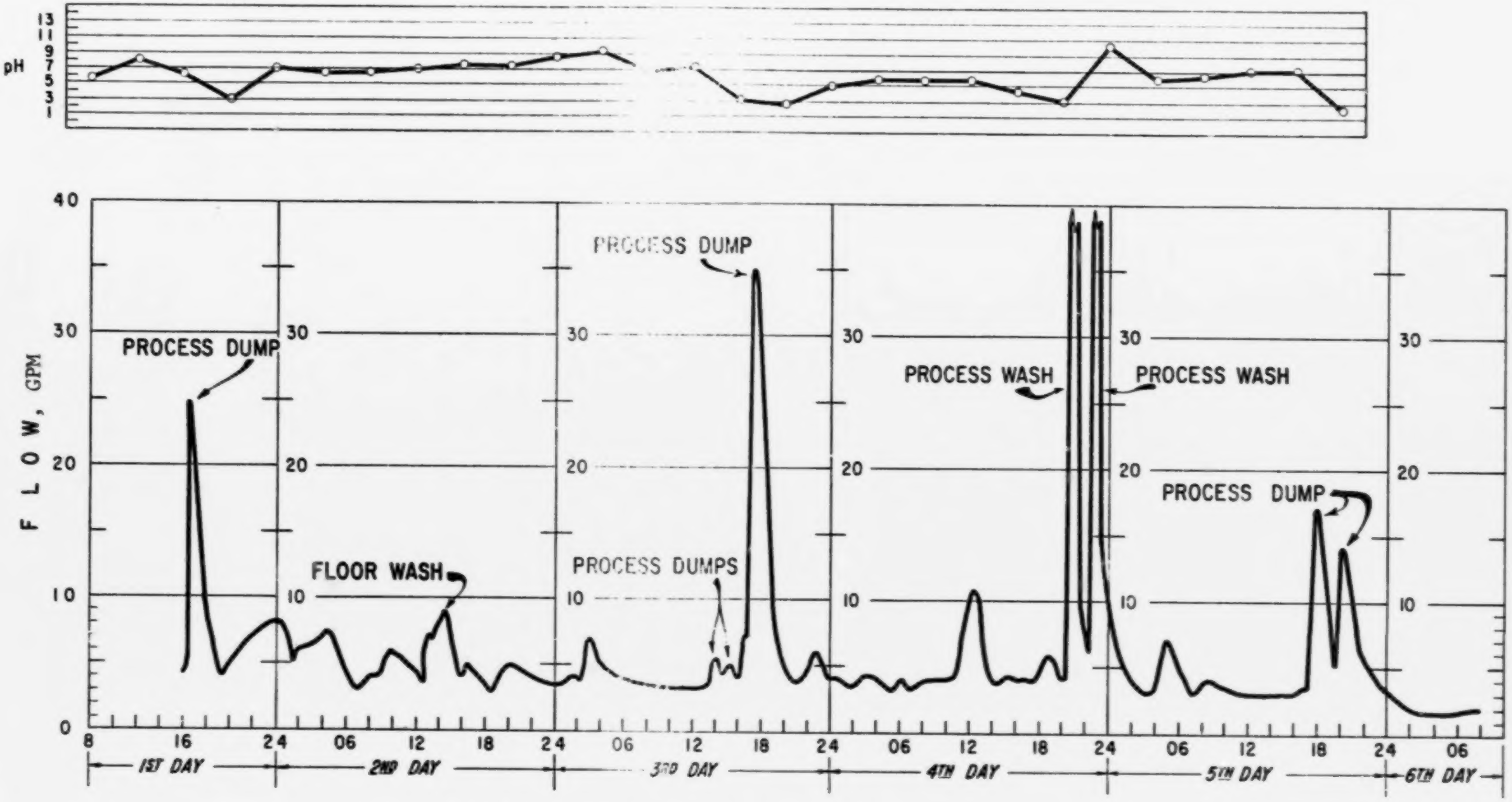


FIGURE 5

FLOW VARIATIONS RESULTING FROM BATCH UNIT PROCESS OPERATION IN A PETROCHEMICAL INDUSTRY

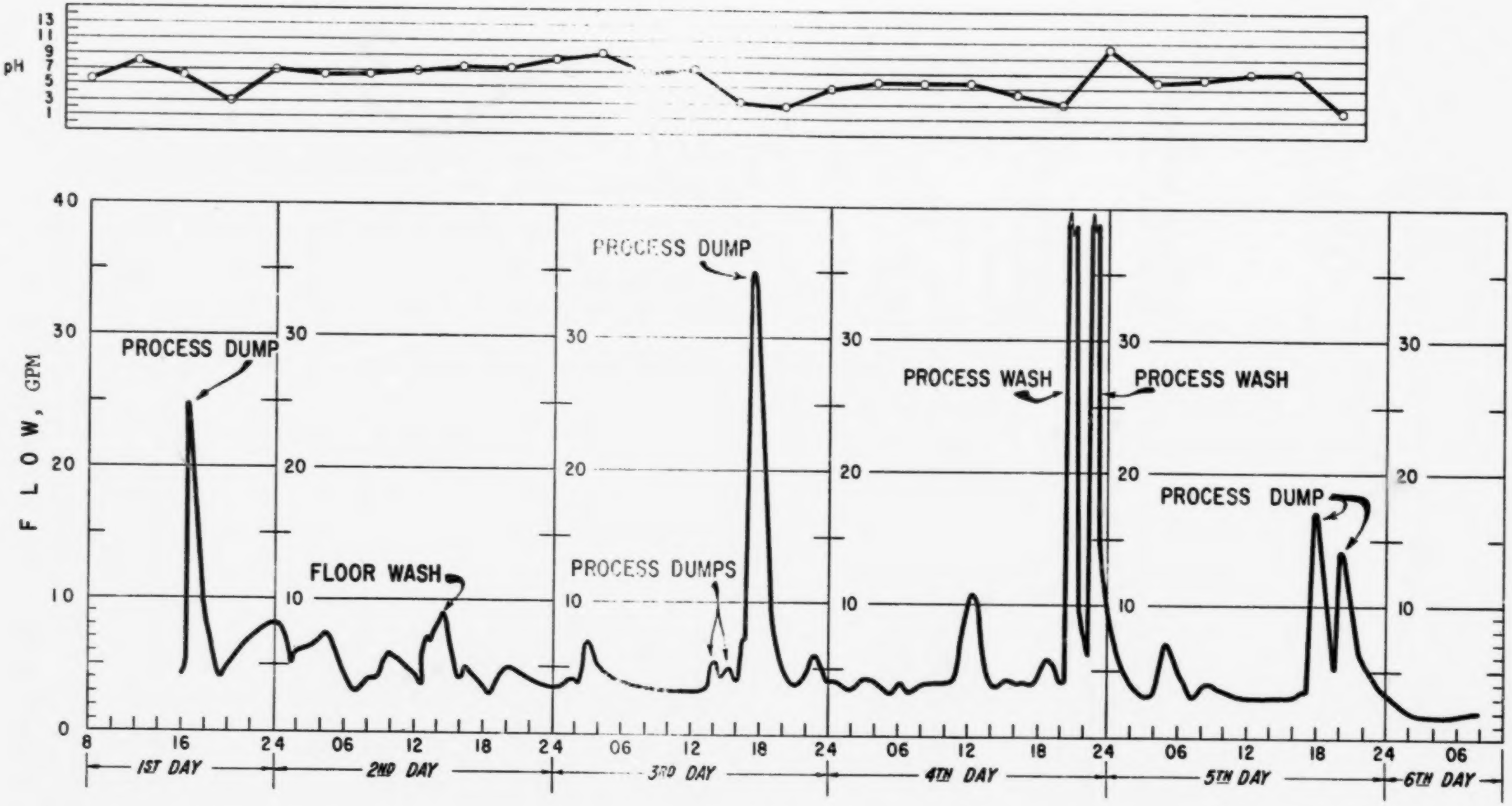


FIGURE 5

FLOW VARIATIONS RESULTING FROM BATCH UNIT PROCESS OPERATION IN A PETROCHEMICAL INDUSTRY

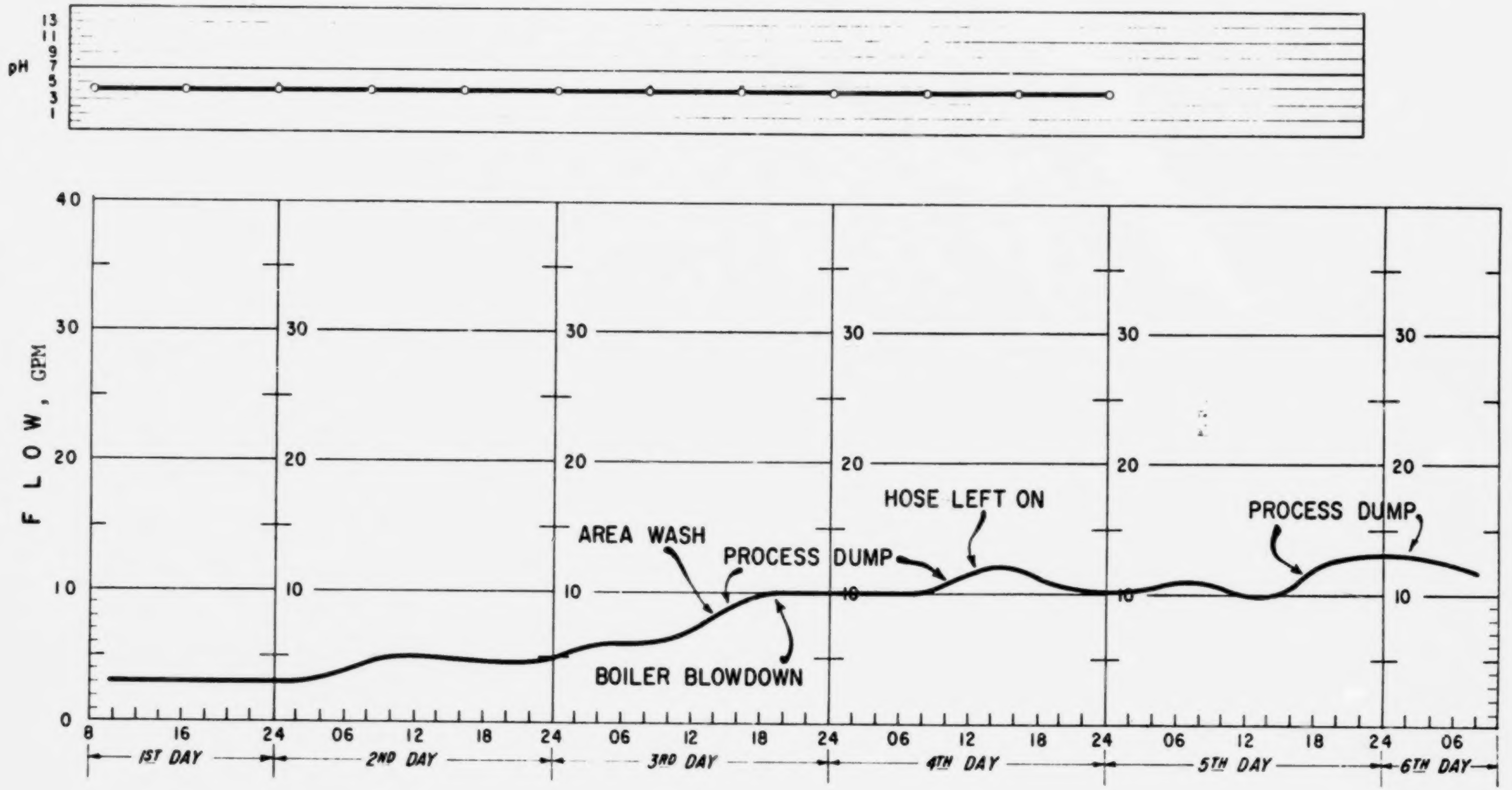


FIGURE 6

OBSERVED FLOW VARIATIONS FOR PROCESS EFFLUENT SHOWN IN FIG. 5 AFTER EQUALIZATION BASINS.

## TABLE 6

## STORM OCCURRENCE AND QUANTITY OF RUNOFF FROM A PETROCHEMICAL INDUSTRIAL AREA*

| Recurrence Interval (Years) | Total 24-Hour Rainfall (Inches) | Estimated Total Runoff (Gals.) |
|---|---|---|
| 1 | 4.05 | 427,900 |
| 2 | 5.35 | 565,300 |
| 5 | 7.25 | 766,000 |
| 10 | 8.7 | 919,200 |
| 25 | 10.05 | 1,061,800 |

*Runoff Coefficient Taken To Be 0.95; Approximate Drainage Area is 13 Acres

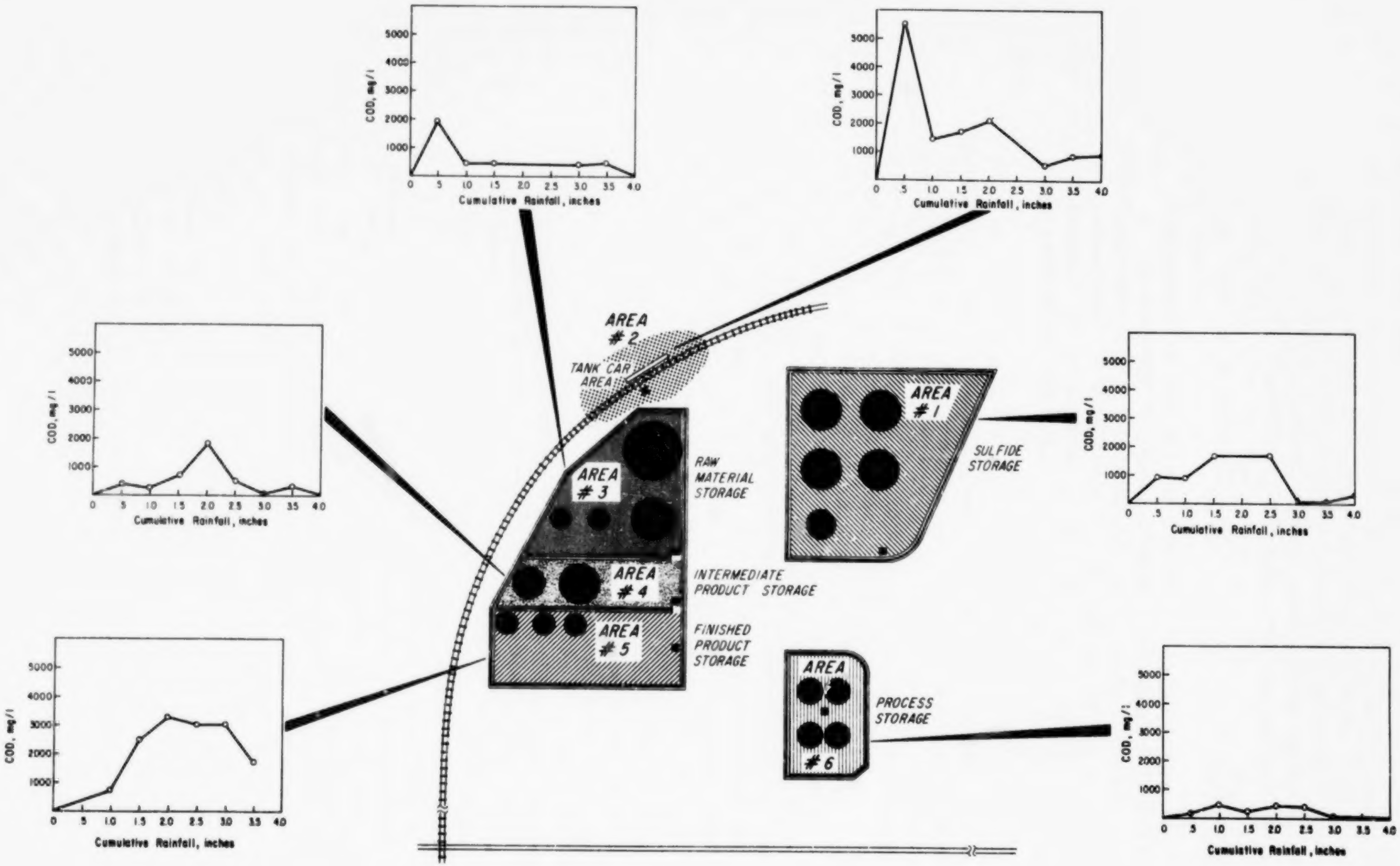


FIGURE 7

ORGANIC CONTAMINATION OF RUNOFF

## PROGRAMMING AN INDUSTRIAL WASTEWATER SURVEY

An industrial wastewater survey should be planned and organized to obtain the maximum amount of significant data with a minimum expenditure of time and money. The survey must include proper sampling techniques at the right locations, sufficient analyses to characterize major pollutants, and be conducted for a sufficiently long period of time to provide reliable statistical inferences.

### Sampling Techniques

The most comprehensive wastewater survey may be programmed and completed with a gross misrepresentation of wastewater characteristics unless proper care is taken to choose the correct sampling techniques. The chosen technique must meet two basic requirements: the sample must be homogenous and representative of the mass sampled, and it must be sufficient for subsequent laboratory examination.

Methods of obtaining samples can be generally classified into two categories; instantaneous or grab samples, and integrated or composite samples. A grab sample is a portion of the waste singularly collected and used as a spot check of the characteristics of the wastewater. In instances where there is a minimal variation of waste characteristics, a grab sample can give sufficient representation. Numerous grab samples can be used to trace the waste variations with proper consideration of sample volume regarding both analyses requirements and volume required for compositing in proportion to flow. Note that compositing techniques should include thorough mixing of each grab sample while compositing to prevent sedimentation of solids.

Continuous sampling is necessary where the waste fluctuates rapidly over a relatively long period of time. Continuous sampling over a 24-hour period is usually adequate, except for waste from "batch dumps" and "turn-arounds" typical of the refinery and petrochemical industries. Periodic grab samples correlated with flow measurements will usually be adequate to describe waste from intermittent sources such as "batch dumps." Continuous samples may be collected automatically in proportion to the flow and composited in one container or the continuous sample may be segregated on an hourly basis (or otherwise, depending on the wastewater characteristic variation). Continuous compositing will yield an "average" wastewater and is adequate where variations are minimal. If, for example, the pH is low half the time and high for the balance of the flow period, a continually composited sample may indicate a neutral waste. In these instances, a segrated composite sample is necessary.

The strict definition of a semi-continuous sample taken over 24 hours, i.e., a "24-hour composite sample", may be given as follows (California, 1965): "24-hour composite sample" means an influent or effluent sample composed of individual grab samples mixed in proportions varying not more than plus or minus 5 percent from the instantaneous rate of waste flow corresponding to each grab sample. These are collected at regular intervals, not greater than 1 hour, throughout any period of 24 consecutive hours, or collected by the use of continuous automatic sampling devices capable of attaining the proportional accuracy stipulated above.

A "grab sample" may be defined as an influent or effluent sample collected at any time from any point at which the sample will contain all wastes discharged through the outfall(s), or a receiving water sample collected at any time from any point in the receiving waters.

Numerous automatic continuous sampling devices can be either purchased or constructed on site. Perhaps the least complicated is where a continuous sample is pumped into containers which are changed automatically for a predetermined time period. Composite samples can be obtained using this sampling method and a concurrent record of the flow.

In cases where the waste stream is hard to reach, where economics demand the most inexpensive approach, and less exact data is required, the simple sampling setup known as the tipping bucket may be applied. This continuous sampling device is one of the most efficient and inexpensive methods of obtaining accurate flow information while obtaining a proportionate sample. In this method, a container is constructed such that the center of gravity shifts and causes the bucket to empty itself when the waste fills the vessel. Each dump is measured by a mechanical counter to give the flow variation with time. A small built-in sampling device fills each time the container fills and empties when the container tips. The proportionate sample may either be composited in one vessel or segregated for individual analyses. This method is easily adapted to waste flows of 0.1 to 20 gpm.

In order to insure the homogeneity of the sample, it is best to obtain it in areas of maximum turbulence or mixing. Withdrawing the sample in the proximity of hydraulic jumps or turbulent areas in sewers or collection systems, for example, enhances the "representativeness" of the sample. As many petrochemical and refinery effluents have both settleable and floatable materials, it is particularly important that these substances be considered when collecting and analyzing the sample. For example, the external mixing of quiescent sampling points should precede the actual withdrawing of the sample in order to minimize the effects of this separation. In some instances when the organic concentration of a sample exclusive of floating oily material is desired, the floating materials in the container can be skimmed off and the remaining aliquot analyzed for organic content.

### Location of Sampling Stations

There is no specific format for locating sampling stations although the following criteria influence the site selection:

1. accessibility;
2. flow measuring potential;
3. wastewater streams included at the sampling point; and,
4. degree of wastewater homogeneity in the sampling area.

Moreover, the site selection should be commensurate with the objectives of the survey, vis, in-plant control and stream segregation, optimal routine of wastewaters with respect to treatment and discharge to receiving bodies of water, evaluating reuse potential, etc. Additionally, more intense sampling should be undertaken in plant areas where concentrated pollutants are anticipated and where wastewater flow and concentration are highly fluctuative.

### Survey Analytical Information

Once the sampling equipment has been selected, the proper techniques developed, and the locations determined, the necessary analyses for each sampling station should be tabulated. This must be done judiciously as too many analyses often overburden the laboratory and the budget without enhancing the effectiveness of the survey. Conversely, infrequent or insufficient sampling can result in data gaps which severely emasculate the overall pollution control program. It is therefore necessary to outline an analytical schedule which is consistent with the stated objectives of the survey. An example of a schedule for a comprehensive sampling program is shown in Table 7. Although individual industrial surveys should be modified as required to meet specific conditions, the format shown in Table 7 can be used as a general guideline.

## SAMPLE PRESERVATION

The applicability of the results of any wastewater characterization or treatability study is necessarily based on the "representativeness" of the samples collected. Moreover, the results depend on the manner in which the samples are preserved during the sampling-analysis time lag. Unpreserved samples may undergo changes resulting from chemical reactions, biological activity, and volatilization. However, even in light of these recognized problems, research has failed to perfect a universal treatment method, or to formulate a set of fixed rules applicable to samples of all types (ASTM, 1966).

## TABLE 7

## SCHEDULE FOR OBSERVATION, SAMPLE COLLECTION, MEASUREMENT, AND ANALYSIS

| Sample Source | Sampling Station | Type of Sample | | | Standard Observations | pH | Dissolved Sulfide - mg/1 | Set. Matter ml/1/hr | Susp. Solids mg/1 | COD, mg/1 | BOD mg/1 | Grease | Nitrogen - mg/1 N | | | | | Phos-phates mg/1 $PO_4$ | | Toxicity 96-Hour Bioassay | Temperature, °C | Dissolved Oxygen - mg/1 | Coliform Organ. MPN/100 ml | Phenol, mg/1 | Chromium, mg/1 | Copper, mg/1 | Lead, mg/1 | Zinc, mg/1 | $NH_4OH$, mg/1 | Undissociated $H_2S$, mg/1 | Special Observations |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Grab | Composite | Flow (MGD) | | | | | | | | mg/1 | $NO_3$ - N | $NO_2$ - N | $NH_3$ - N | Organic-N | Total - N | Ortho-phosphate | Total Phosphate | % Survival in Waste (undil.) | | | | | | | | | | | |
| Effluents | 1 | X | | M | M | | | | | M | Q | | | | | | | | | | | | | | | | | | | | |
| " | 2 | X | | | W | W | W | W | | | | W | | | | | | | | | W | W | | | | | | | | M | |
| " | 2 | | X | C | | | | | W | W | W | W | Q | Q | Q | 2/M | Q | Q | Q | M | W | W | 2/W | M | Q | Q | Q | Q | Q | Q | |
| " | 4 | X | | 1,2<br>M | | | | | | E | | | | | | | | | | | | | | | | | E | | | | |
| " | 5 | X | | 1,2<br>M | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| " | 6 | X | | 3<br>M | M | M | M | 4<br>M | 4<br>M | 4<br>M | | | | | | | | | | | | | | | | | | | | | |
| Intake | 3 | X | | | | W | W | W | | W | | | | | | | | | | | W | | 2/W | | | | | | | | |
| " | 3 | | X | D | | W | | W | W | W | | | | | Q | | | | | | | | | | Q | Q | Q | Q | Q | | |
| Receiving | 7-17 | X | | | 2/M | | Q | | | M | M | | Q | Q | Q | Q | Q | Q | Q | 2/Y | 2/M | 2/M | | Q | Q | Q | Q | Q | Q | Q | |
| Bottom Sediment | | | X | | 2/Y | | | | | | | 2/Y | | | | | | | | | | | | | | | | | | | 2/Y |

C = Continuous Measurement
W = Once Weekly
2/W = Twice Weekly
M = Once Monthly

2/M = Twice Monthly
Q = Once Quarterly
2/Y = Twice Yearly
E = Each Time Runoff or Discharge Occurs

1 = Monthly log of deposited waste to include data and quantity of disposal.
2 = Monthly log showing data, quantity, and point of disposal for all waste hauled away.
3 = Estimated average daily flow at time of sampling.
4 = Sampling and analyses required during the rainy season.

In general, the most common preservation methods include acidification, refrigeration without freezing, and freezing. However, any one of these methods will not maintain a sample in a static condition for long periods of time. For example, the inorganic and organic composition of a sample containing microorganisms may be altered merely as a result of freezing and thawing. The microorganisms act as "bags" of impermeable membranes until they are disrupted by freezing and thawing, thus passing their dissolved materials into solution. Also, biochemical changes such as nitrification continue in frozen samples of mixtures of algae and bacteria at concentrations as low as 5 to 10 mg/l (Jewell, 1968). The best overall rule with respect to preservation is to complete the analyses as soon as possible. Probable errors due to deterioration of the sample should be designated in reporting the analytical data.

Several studies have compared the effectiveness of acidification, refrigeration, and freezing on samples (Paulson, API; Agardy & Kiado, 1966; Jewell, 1968; FWPCA, 1969). Procedures for preserving organic wastewaters including domestic aqueous wastes are presented in Table 8.

Special care should be exercised when preserving refinery wastewaters. For example, the characteristic burnt sulfide odor in refinery wastewater is more intense in an acidified sample than in a frozen sample (Little, 1967), with the odor of the acidified sample more characteristic of freshly collected samples. Paulson (1969) reported that the recognizable odor number of frozen samples was half that of acidified samples and that considerable difficulties are always encountered in attempting to transport frozen samples to the laboratory. It has also been demonstrated that preservation by freezing and acidification did not completely inhibit bacterial reproduction as indicated by bacterial counts.

Where total and dissolved concentrations are to be determined, emphasis should be placed on the separation technique. Dissolved material may be considered to be that which passes a 0.45 micron membrane filter (FWPCA, 1969). When the dissolved concentration is to be determined, filtration should be carried out as soon as possible in the field or as soon as it is received in the laboratory. Filtration of the sample may result in loss of the organics on the container surfaces or the filter material. Volatile material may be lost if the sample is filtered under a vacuum. Therefore, care should be exercised to insure that pollutants are not inadvertantly removed during sample handling.

Although it is generally agreed that detailed handling and preservation methods cannot be given for all wastewaters because of widely varying characteristics, the Federal Water Quality Administration laboratories have provided general guidelines for the preservation of samples for several analyses. The parameter measured, method of preservation, and maximum holding period are summarized in Table 9.

TABLE 8

## RECOMMENDED STORAGE PROCEDURE

(Agardy and Kiado 1966)

| Analysis | Sample Storage | |
|---|---|---|
| | Refrigeration @ 4°C | Frozen |
| Total Solids | OK | OK |
| Suspended Solids | Up To Several Days | NO |
| Volatile Suspended Solids | Up To Several Days | NO |
| COD | Up To Several Days | OK |
| BOD | Up To One Day In Composite Sampling Systems | Lag Develops, Must Use Fresh Sewage Seed |

TABLE 9

## SAMPLE PRESERVATION

(FWPCA, 1969)

| Parameter | Preservative | Maximum Holding Period |
|---|---|---|
| Acidity-Alkalinity | Refrigeration at 4°C | 24 hours |
| Biochemical Oxygen Demand | Refrigeration at 4°C | 6 hours |
| Calcium | None Required | --- |
| Chemical Oxygen Demand | 2 ml Conc $H_2SO_4$/liter | 7 days |
| Chloride | None Required | --- |
| Color | Refrigeration at 4°C | 24 hours |
| Cyanide | NaOH to pH 10 | 24 hours |
| Dissolved Oxygen | Determine on Site | No Holding |
| Fluoride | None Required | --- |
| Hardness | None Required | --- |
| Metals, Total | 5 ml Conc $HNO_3$/liter | 6 months |
| Metals, Dissolved | Filtrate: 3 ml 1:1 $HNO_3$/liter | 6 months |
| Nitrogen, Ammonia | 40 mg $HgCl_2$/liter - 4°C | 7 days |
| Nitrogen, Kjeldahl | 40 mg $HgCl_2$/liter - 4°C | Unstable |
| Nitrogen, Nitrate-Nitrite | 40 mg $HgCl_2$/liter - 4°C | 7 days |
| Oil and Grease | 2 ml Conc $H_2SO_4$/liter - 4°C | 7 days |
| Organic Carbon | 2 ml Conc $H_2SO_4$/liter (pH 2) | 7 days |
| pH | None Available | --- |
| Phenolics | 1.0 g $CuSO_4 + H_3PO_4$ to pH 4.0 - 4°C | 24 hours |
| Phosphorus | 40 mg $HgCl_2$/liter - 4°C | 7 days |

TABLE 9 (Cont)

SAMPLE PRESERVATION

| Parameter | Preservative | Maximum Holding Period |
|---|---|---|
| Solids | None Available | --- |
| Specific Conductance | None Required | --- |
| Sulfate | Refrigeration at 4°C | 7 days |
| Sulfide | 2 ml Zn Acetate/liter | 7 days |
| Threshold Odor | Refrigeration at 4°C | 24 hours |
| Turbidity | None Available | --- |

## ORGANIC ANALYSES - COD, BOD, TOC, TOD

Organic wastewater samples should be collected and stored in glass bottles or in containers that will not interfere with the analysis of the parameter of interest, either in a positive or a negative manner, i.e., interference by the release of organic material to solution or adsorption and absorption of organics by container surfaces.

Traces of organic material from glassware or the atmosphere may cause high, positive errors in the COD analysis. Therefore, care should be taken to exclude contaminants. Glassware may be conditioned by running blank procedures to eliminate traces of organic material. With proper precautions, the COD analysis is accurate at concentrations as low as 20 mg/l with a standard deviation of 10 percent of the average.

The loss of volatile materials because of the heat rise upon addition of the concentrated $H_2SO_4$ should be noted.

In all samples where organic material is being analyzed, it is essential to complete the analysis as soon as possible. This is imperative with biologically active material. In cases where it is not possible to measure the organic carbon within 2 hours, it is necessary to acidify the samples.

## Oil and Grease

Samples should be collected in wide mouth bottles with a volume of at least one liter. Care should be exercized in handling the sample in order to prevent loss of oily materials prior to analysis.

## Color and Turbidity

These two parameters are closely related. Samples with biologically active material should be analyzed as soon as possible as both color and turbidity sometimes change with sample age.

## Dissolved Oxygen

This analysis must be completed as soon as possible after sampling, especially when oxygen utilizing chemicals such as ferrous iron or sulfides are present. If analysis must be postponed, the sample may be preserved by "fixing" the samples with the first two reagents used in this test; i.e., by addition of the $MnSO_4$ and alkalide-azide reagents. It is recommended that the analysis be completed within 4 to 8 hours after preservation in this manner.

## Nitrogen and Phosphorus

It is extremely difficult to retard the nitrogen and phosphorus cycles by any preservation technique in samples containing organic material. However, if it is necessary to measure particulate and dissolved forms, the first step for preservation would be separation of particulates in one preserved sample. This will reduce the effect of particulates on the parameter of interest during the preservation period. Analysis of total Kjeldahl nitrogen and phosphorus should be completed on separate samples. The most effective method of retarding the rate of conversions in the nitrogen and phosphorus cycles is by inhibiting the growth of microorganisms by the addition of 40 mg/l $HgCl_2$ (using a one percent solution) and storing at 4°C.

## Activated Sludge Mixed Liquor

In pilot plant studies of activated sludge, it is desirable to use a "standardized" activated sludge. However, it is not feasible to maintain a constant activated sludge culture in a functioning condition for extended periods of time. Changes in the composition and activity of the sludge takes place continuously and upsets are likely to occur. For these reasons, methods of preserving activated sludge have been evaluated (Buzzell, Thompson, and Ryckman, 1969). The following preservation methods were tested with regard to the practicability and the character (washing response appearance) of the sludge after preservation:

1. Freezing slowly at -15°C (deep-freezer uni.,
2. Freezing quickly at -76° (acetone and dry ice)
3. Freezing quickly at -192°C (liquid nitrogen)
4. Lyophilization

In all cases, lyophilized (freeze-dried) sludge was the most vigorous, using oxygen at a significantly higher rate than sludges preserved by the other methods.

The general method of preservation by lyophilization and reactivation is outlined as follows:

1. The solids are concentrated by centrifuging at 870 G to a concentration of 80,000 to 100,000 mg/l.

2. The concentrated sludge is quickly frozen in an acetone dry ice bath at -78° ± 2°C, and then attached to a refrigerated vacuum unit where the water is removed by sublimation over a period of 24 hours.

3. Before using the sludge, it is necessary to add moisture to rejuvenate the microorganisms. Moisture is added by mixing a weighed amount of the dried sludge with synthetic sewage. The sludge is placed in batch units and fed twice daily. It has been found that 24 hours of rejuvenation were necessary to obtain maximum reaction rates.

Sludge preserved in the manner prescribed above can be stored in a screw-top bottle, unrefrigerated in the dark for at least 6 months as long as the sample is free of moisture. Sludge in this form is easily handled and weighed and is reportedly not affected by hygroscopic moisture during weighing. No problems have been experienced in re-suspending the dried sludge and its appearance is very similar to that observed prior to lyophilization.

Before wastewater samples are fed to treatability units or subjected to most chemical analyses, preservation constraints must be removed; i.e., acidified samples neutralized, frozen samples reactivated, and refrigerated samples warmed to room temperature. If wastewater temperatures are expected to deviate from room temperature, appropriate adjustment should be made prior to their use in treatment units.

## SAMPLE VOLUME REQUIREMENTS

Wastewater sample volumes depend on the type and number of determinations to be made and the size and retention time of the treating unit under investigation. Generally, at least 2 to 3 liters should be collected and an additional liter if all mineral constituents are to be analyzed. The quantity collected should include a surplus for verifying analyses and for performing additional analyses. It is difficult to predict sample requirements necessary for the treatability studies since any combination of physical, chemical and biological treating units may be used.

Approximations of volume requirements for several analyses are available from ASTM (ASTM, 1966). After these factors are estimated, it is customary to increase the sample size by a safety factor to account for underestimates, reruns, and additional testing which may become necessary after initial investigation.

Confirmatory analyses should be conducted to detect any changes in the wastewater between sampling and testing, especially where long hauling distances are involved. Ground transportation is normally the most economical means of shipping bulk samples and truck and bus lines offer relatively fast and efficient service in most areas of the United States. A successful treatability study is dependent upon several factors, many of which have been previously discussed; but nothing is more important than performing all pertinent analyses on representative samples. The conjunctive use of sample preservation and/or coordinated sample scheduling are prerequisites for a valid treatability study.

# WASTEWATER CHARACTERIZATION

## INTRODUCTION

A comprehensive analytical program for characterizing wastewaters must be based on relevancy to unit treatment process operations and effluent quality constraints. It is therefore necessary to consider these unit processes in terms of the effect specific pollutants have on their operational effectiveness as well as their process capacity relative to satisfying effluent quality criteria. Once this has been accomplished, a characterization schedule consistent with the goals of the program for identifying and treating refinery and petrochemical wastewaters can be formulated. The characterization of treatment processes, but also serves as the basis for delineating contaminated and uncontaminated streams within a plant, identifying toxic streams, and indicating streams with reuse or product recovery potential. A general analytical format for characterizing the organic and inorganic constituents in wastewaters is illustrated in Figure 8.

## PARAMETER APPLICATION FOR THE CHARACTERIZATION OF WASTEWATERS

Parameters used to characterize the liquid and sludge fractions of petrochemical and refinery wastewaters can be categorized into organic and inorganic analyses. The organic content of wastewater usually is estimated in terms of oxygen demand using biochemical oxygen demand (BOD), chemical oxygen demand (COD) or total oxygen demand (TOD), or in terms of carbon using total organic carbon (TOC). The interrelationship of these organic parameters in terms of accuracy (yield in terms of percent of theoretical oxygen demand or carbon concentration) is shown in Figure 9.

It should be recognized that these parameters do not measure the same constituents. Specifically, they may be defined as meaning the following:

BOD - biodegradable organics (in terms of oxygen demand)

COD - organics which can be oxidized chemically and some inorganics such as sulfides, sulfites, ferrous iron, chlorides, and nitrite.

TOD - all organics and some reduced inorganics (in terms of oxygen)

TOC - all organic carbon (in terms of carbon)

Other organic analyses commonly used in the characterization of refinery and petrochemical wastewaters include organic acids, alcohols, aldehydes, phenolics, oils, etc.

The inorganic characterization schedule should include those tests which provide information concerning:

1. potential toxicity (heavy metals, etc.)
2. potential inhibitors (chlorides, sulfates, etc.)

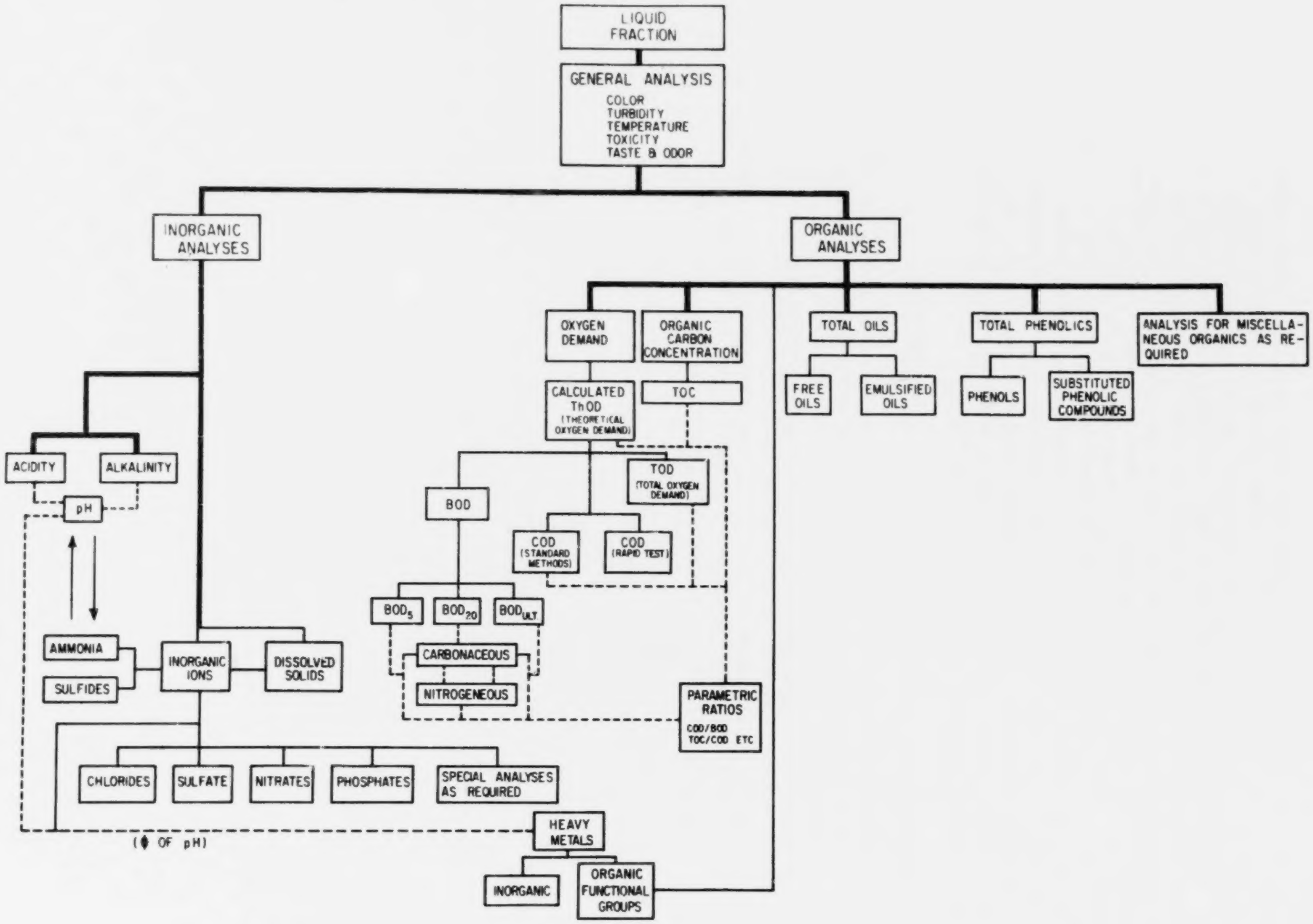

LIQUID FRACTION
GENERAL ANALYSIS
COLOR
TURBIDITY
TEMPERATURE
TOXICITY
TASTE & ODOR
INORGANIC ANALYSES
ORGANIC ANALYSES
ACIDITY
ALKALINITY
pH
AMMONIA
SULFIDES
INORGANIC IONS
DISSOLVED SOLIDS
CHLORIDES
SULFATE
NITRATES
PHOSPHATES
SPECIAL ANALYSES AS REQUIRED
HEAVY METALS
(ϕ OF pH)
INORGANIC
ORGANIC FUNCTIONAL GROUPS
OXYGEN DEMAND
ORGANIC CARBON CONCENTRATION
CALCULATED ThOD (THEORETICAL OXYGEN DEMAND)
TOC
TOD (TOTAL OXYGEN DEMAND)
BOD
COD (STANDARD METHODS)
COD (RAPID TEST)
BOD5
BOD20
BODULT
CARBONACEOUS
NITROGENEOUS
PARAMETRIC RATIOS
COD/BOD
TOC/COD ETC
TOTAL OILS
FREE OILS
EMULSIFIED OILS
TOTAL PHENOLICS
PHENOLS
SUBSTITUTED PHENOLIC COMPOUNDS
ANALYSIS FOR MISCELLANEOUS ORGANICS AS REQUIRED

FIGURE 8

CHARACTERIZATION OF LIQUID WASTEWATER

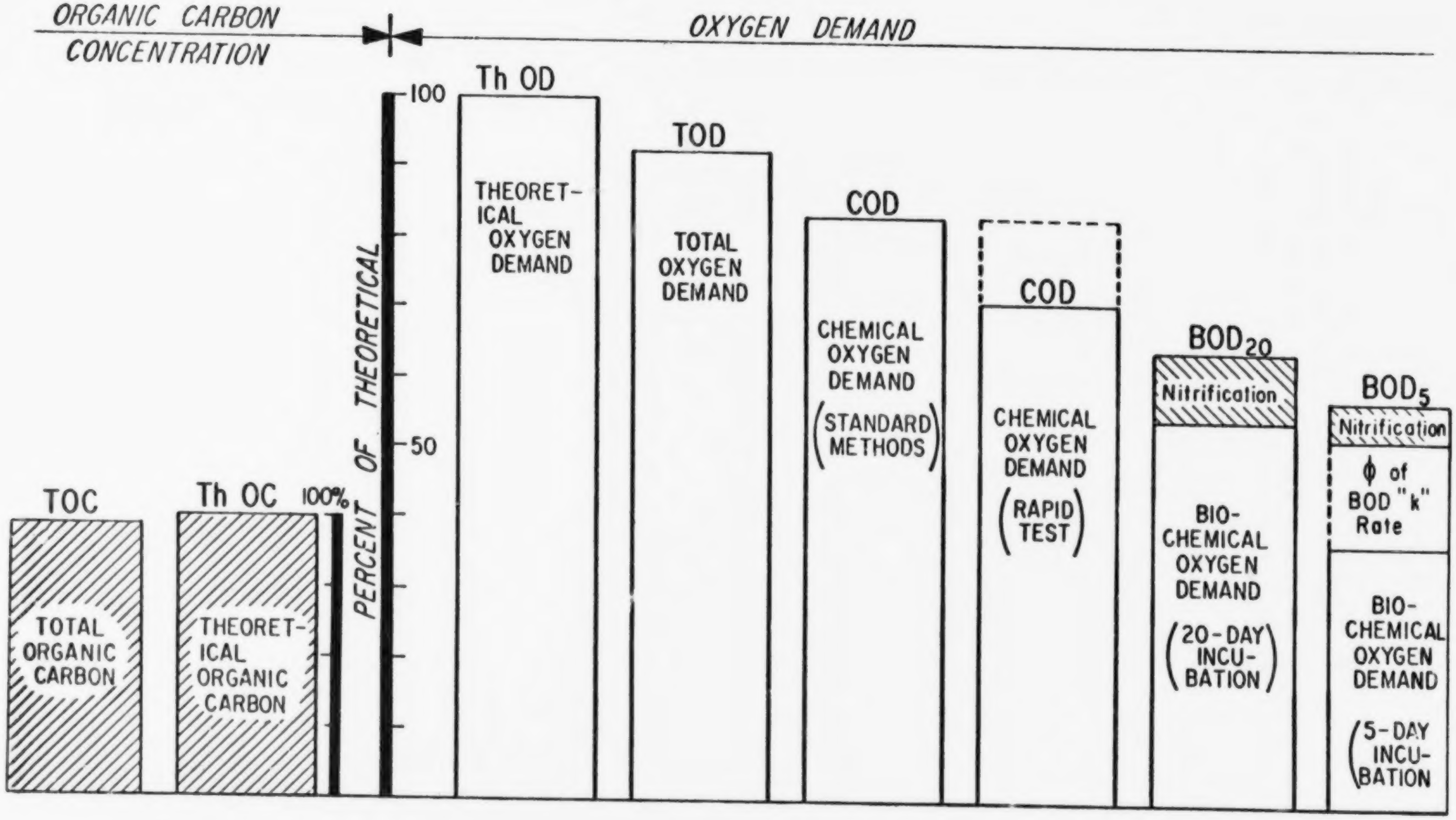

ORGANIC CARBON CONCENTRATION
OXYGEN DEMAND
PERCENT OF THEORETICAL
100
50
100%
TOC
TOTAL ORGANIC CARBON
Th OC
THEORET-ICAL ORGANIC CARBON
Th OD
THEORET-ICAL OXYGEN DEMAND
TOD
TOTAL OXYGEN DEMAND
COD
CHEMICAL OXYGEN DEMAND (STANDARD METHODS)
COD
CHEMICAL OXYGEN DEMAND (RAPID TEST)
BOD20
Nitrification
BIO-CHEMICAL OXYGEN DEMAND (20-DAY INCU-BATION)
BOD5
Nitrification
ϕ of BOD "k" Rate
BIO-CHEMICAL OXYGEN DEMAND (5-DAY INCU-BATION)

FIGURE 9

RELATIONSHIP BETWEEN OXYGEN AND CARBON PARAMETERS

(Ford, et al 1970)

3. contaminants necessitating specified treatment (acidity or alkalinity, pH, suspended solids, *etc.*), and

4. nutrient evaluation (nitrogen and phosphorus)

When considering wastewater characterization, organic and oxygen-demanding substances are of immediate concern. However, the single and conjunctive use of many parameters, both organic and inorganic, may be necessary to provide the proper analysis of a wastewater. A review and discussion of the aforementioned parameters is included as follows.

## Organic Parameters

### Biochemical Oxygen Demand (BOD)

The BOD is an estimate of the amount of oxygen required to stabilize biodegradable organic materials by a heterogeneous microbial population. The procedures for performing the BOD test are described in *Standard Methods for the Examination of Water and Wastewater* (1965). The BOD, however, is subject to many variables and constraints, particularly when considering complex industrial wastes (Eckenfelder and Ford, 1970). These are discussed as follows.

### Time of Incubation

The importance of the incubation time variable is indicated in the basic BOD equation. The usual time is taken as five days although the time for complete stabilization to occur (the ultimate BOD) will depend on the nature of the substrate and the viability of the seed microorganisms. Many substrates can be substantially degraded in twenty days and the twenty-day BOD is considered as the ultimate BOD in various applications. For example, the ultimate oxygen demand in many receiving bodies of water is predicated on twenty-day values, and the effluent quality criteria is therefore expressed in terms of twenty-day BOD. It should be recognized, however, that many organic compounds require longer periods of time before the ulimate oxygen demand is satisfied biologically. Recently published BOD curves for tertiary butyl alcohol using acclimated seed indicated that 2 percent of the theoretical yield occurred in 5 days, approximately 65 percent occurred in 20 days, and the ultimate demand was satisfied in excess of 30 days (Love, 1970). Assuming these data are valid, the oxygen requirement for a long-term biological detention basin receiving substantial quantities of TBA would be underestimated if based on 5-day or 20-day BOD values. This underscores the importance of properly assessing the BOD time variable with respect to the ultimate oxygen demand.

### Nitrification

During the first 5 to 10 days, the oxygen demand is generally exerted by carbonaceous materials with a second stage demand being exerted by nitrogeneous materials. The nitrification rate constants are much lower than those for carbonaceous destruction; and, although the 2 reactions may occur simultaneously, the nitrification demand is not normally conspicuous until the carbonaceous demand has been substantially satisfied. A graphic representation of these reactions is shown in Figure 10. The measurement of oxygen demand exerted by the carbonaceous fraction of the waste can be made in 1 of 2 ways, namely: by retarding nitrification in the test bottle by the addition of nitrifying inhibitors, or by allowing nitrification to occur and subtracting its demand from the overall result.

### Temperature and pH

Although most BOD tests are performed at the standard temperature of 20°C, field conditions often necessitate incubation at other temperatures requiring correction factors to compensate for the temperature difference (Schroepfer, 1964). Similarly, a pH adjustment is required if the acidity or alkalinity of the sample is sufficient to create a pH outside the range of 6.5 to 8.3 in the BOD bottle (Eckenfelder and Ford, 1970).

### Seed Acclimation

The use of a biological seed which is not properly acclimated to the test wastewater is probably the factor most commonly responsible for erroneous BOD results. A biological seed should be developed in a continuous or batch laboratory reactor, feeding the diluted wastewater to the initial microbial seed. The waste composition is increased to full strength over a period of time; and once the organic removal or oxygen uptake in the reactor reaches the maximum level, the seed can be considered as acclimated. The time required to obtain this acclimation depends on the nature of the seed and wastewater. For domestic wastewaters or combined industrial-domestic wastes, the period should be less than 1 week. However, for wastes containing high concentrations of complex organic compounds such as those present in refinery or petrochemical wastes, a period of several weeks may be required.

### Toxicity

The presence of toxic materials in a wastewater sample may have a biotoxic or biostatic effect on seed microorganisms. The effect is usually evidenced by "sliding" BOD values where the BOD yield increases with increasing sample dilution. Once there is the indication of the presence of toxic materials, steps should be taken to identify and remove the toxicants or use dilution values above which the BOD yields are consistent.

## Chemical Oxygen Demand (COD)

The COD is a measure of the oxygen equivalent of those constituents in a sample which are susceptible to permanganate or

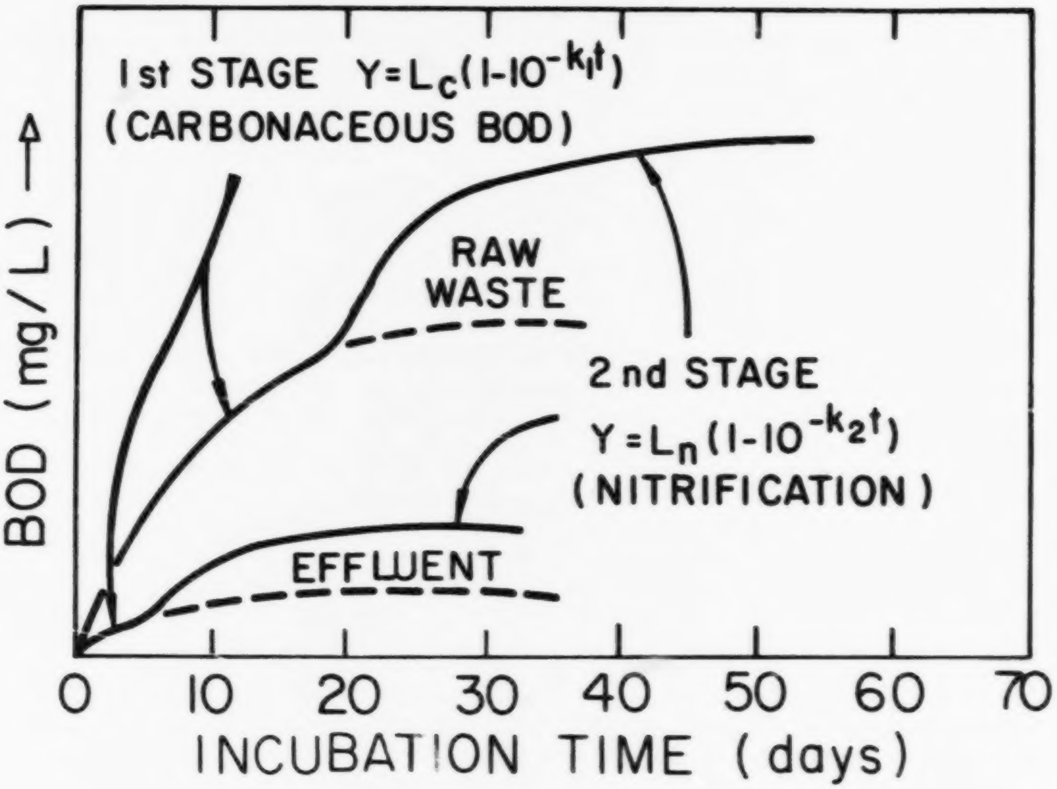


FIGURE 10

BIOCHEMICAL OXYGEN DEMAND

dichromate oxidation in an acid solution. Although it is independent of many of the variables which affect the BOD test, there are still factors which influence the COD value of the sample in question.

Generally, one would expect the ultimate BOD of a wastewater to approach its COD value. There are several factors, however, which prevent a consistent BOD ult/COD ratio of unity. These include:

1. Many organic compounds are dichromate or permanganate oxidizable but are resistant to biochemical oxidation.

2. The BOD results may be affected by lack of seed acclimation, giving erroneously low readings.

3. Certain inorganic substances such as sulfides, sulfites, thiosulfates, nitrites, and ferrous iron are oxidized by dichromate, creating an inorganic COD.

4. Chlorides interfere with the COD analysis but provisions have been made to eliminate this interference.

A modification of the COD test as described in Standard Methods has been applied recently (Jeris, 1967; Foulds and Lunsford, 1968). An aliquot of wastewater sample is added to a dichromate-acid-silver solution and heated to 165°C using a digestion time of 15 minutes. The sample is then diluted with distilled water and titrated with ferrous ammonium sulfate. The COD yield using this approach is approximately 66 percent of the yield using the Standard Methods approach, the exact amount depending on the complexity and stability of the organic constituents involved.

Total Organic Carbon (TOC)

Although TOC is a parameter that has been applied in the field for many years, the advent of the carbon analyzer has provided a rapid and simple method for determining organic carbon levels in aqueous samples, enhancing the popularity of TOC as a fundamental measure of pollution. The organic carbon determination is free of the many variables inherent in COD or BOD analyses, with more reliable and reproducible data being the net result (Eckenfelder and Ford, 1970). The carbon analyzer basically provides for the complete oxidation of organic materials using an analyzer flow diagram as illustrated in Figure11. A carrier gas conveys the sample through a catalytic combustion tube where the constituents are oxidized to carbon dioxide and water. The steam is removed in a condenser and the remaining gas flows through an infrared analyzer sensitized for carbon dioxide detection. The system as shown in Figure11 includes a high temperature combustion tube for total carbon analysis and a low temperature tube for inorganic carbon analysis, the difference taken as total organic

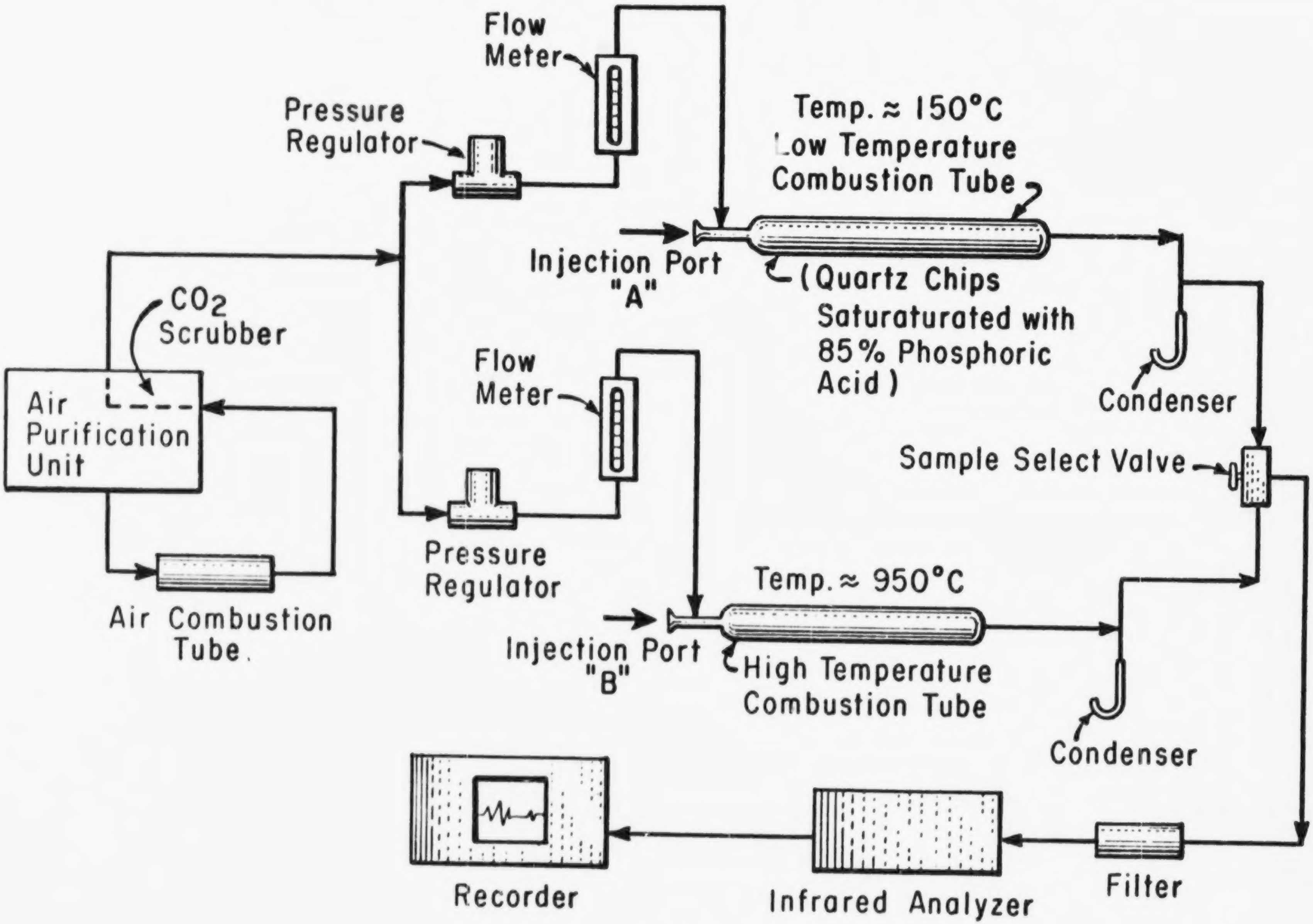

Flow Meter
Pressure Regulator
Temp. ≈ 150°C
Low Temperature Combustion Tube
Injection Port "A"
(Quartz Chips Saturaturated with 85% Phosphoric Acid)
$CO_2$ Scrubber
Air Purification Unit
Flow Meter
Condenser
Sample Select Valve
Pressure Regulator
Temp. ≈ 950°C
Air Combustion Tube.
Injection Port "B"
High Temperature Combustion Tube
Condenser
Recorder
Infrared Analyzer
Filter

FIGURE 11

FLOW DIAGRAM OF MODIFIED CARBON ANALYZER carbon. As the analysis time using the carbon analyzer is only several minutes, the efficacy of using this parameter is apparent, particularly when a TOC-COD or TOC-BOD correlation can be established.

## Total Oxygen Demand (TOD)

Another analyzer has been developed to measure the amount of oxygen required to combust the impurities in an aqueous sample. This measurement is achieved by providing a continuous analysis of the oxygen concentration present in a nitrogen carrier gas. The oxidizable constituents in the liquid are converted to their stable oxides in a platinum catalyzed combustion chamber. This disturbs the oxygen equilibrium at the platinum surface which is restored by the oxygen in the carrier gas stream. This depletion is detected by a silver-lead fuel cell and is recorded as a negative peak related to the oxygen demand of the sample. The TOD method measures the amount of oxygen consumed in the following chemical reactions (CLifford, 1967).

TABLE 10

TOTAL OXYGEN DEMAND REACTIONS

| Reaction | Highest Stable Oxidation State | Percent Reaction Efficiency |
|---|---|---|
| $C + O_2$ | $CO_2$ | 95 - 100 |
| $H_2 + \frac{1}{2}O_2$ | $H_2O$ | 95 - 100 |
| $N^{\pm 3} + \frac{1}{2}O_2$ | NO | 95 |
| $S^{-2} + 2O_2$ | $SO_4^{-2}$ | 78 |
| $SO_3^{-2} + \frac{1}{2}O_2$ | $SO_4^{-2}$ | 72 |

The TOD and TOC analyzers have similar applications, the output data being correlated to COD and BOD values when possible.

## Correlation of Organic Parameters

One of the most effective uses of the aforementioned organic parameters is to consider them in terms of their interrelationships. Each of these parameters should be interpreted not only as an array of individual values, but also as sets of numbers which relate to each other. This approach alludes to a more interpretative definition of the nature of organics which is represented by these analyses.

## COD and BOD Relationships

The COD-BOD relationship is generally considered to indicate the fraction of the chemically oxidizable organics which are amenable to biological degradation. For example, if the BODult/COD ratio of a chemical or refinery wastewater approached unity, a major fraction of the organic materials in the waste would be considered as biodegradable. Conversely, a $BOD_{ult}$/COD ratio of 0.1 to 0.3 would indicate that a major portion of the organics which are amenable to chemical oxidation are resistant to biochemical oxidation, and a proposed biological treatment system should be considered as questionable on this basis. It is, of course, possible that a large fraction of the observed COD is attributable to the oxidation of reduced inorganic constituents, but this can be determined by performing ancillary chemical analyses.

Average $BOD_5$ and COD values for wastewaters discharged from chemical plants producing the indicated products are tabulated in Table 11. More specifically, it is helpful to evaluate the BOD or COD yields as a portion of the theoretical oxygen demand for various classes of compounds. The COD and BOD yields with respect to theoretical oxygen demand (Th OD) for aliphatics, aromatics, nitrogeneous organics, and refractory organics are presented in Table 12 (Buzzell, Young and Ryckman, 1968).

## COD-BOD/TOC Relationships

In attempting to correlate the COD or BOD of a petrochemical or refinery wastewater to TOC, certain factors which might constrain or discredit the correlation should be considered at the outset. These include:

1. A portion of the COD may be attributable to the oxidation of inorganics as previously described while the TOC analysis does not include the oxidation of these compounds.

2. The BOD or COD tests do not include those organic compounds which are partially or totally resistant to chemical or biochemical oxidation. However, all of the organic carbon is recovered in the TOC analysis.

3. The BOD test is susceptible to variables which include seed acclimation, pH, temperature, toxic substances, etc. The COD and TOC tests are independent of these variables.

One would expect the stoichiometric COD/TOC ratio of a wastewater to approximate the molecular ratio of oxygen to carbon (32/12 = 2.67). Theoretically, the ratio limits would range from zero, when the organic material is resistant to dichromate oxidation,

# TABLE 11

## CHEMICAL WASTE CHARACTERISTICS

| Principal Products | Q (mgd) | $BOD_5$ (mg/l) | COD (mg/l) | SS (mg/l) |
|---|---|---|---|---|
| Phthalic anhydride, maleic anhydride plasticisers, $H_2SO_4$ | 0.002 | - | 300 | 24 |
| Chemical warfare gas, chromium plating | 0.001 | 200 | 1100 | - |
| Terephthalic acid, isophthalic acid, dimethyl terephthalate | 5.36 | - | 9800 | 10,600 |
| Butadiene, styrene, polyethylene, olefins | 1.68 | - | - | - |
| Phenol, ethylene | 2.0 | 300 | 1200 | 300 |
| Acrylonitrile | 0.302 | - | 1200 | 238 |
| Fatty acids, esters, glycerol | 0.10 | 10,000 | 14,000 | - |
| Regenerated cellulose | 1.41 | - | - | - |
| Acetylene | - | - | - | - |
| Dyes, pigments, inks | 0.452 | 237 | - | 93 |
| Azo & anthraquinine dyes | 0.94 | 352 | 1760 | 152 |
| Anthraquinine vat dyes | 2.0 | 380 | 1160 | - |
| Ethylene, alcohols, phenol | 5.9 | 1700 | 3600 | 610 |
| Benzene, ethylene, butyl rubber, butadiene, xylene, isoprene | 14.7 | 91 | 273 | - |
| Acrylonitrile, acetonitrile, hydrogen cyanide | 3.9 | 300 | 830 | 106 |
| Terephthalic acid | 0.335 | - | 4160 | - |
| Glycerine, various glycols | 0.49 | 2810 | - | - |
| Methyl & ethyl parathion | 0.075 | 3100 | 5200 | 90 |
| Methyl isocyanate, phosgene diphenol glycine | 0.543 | 1146 | 3420 | - |
| Urea, ammonia, nitric acid, $NH_4NO_3$ | 0.65 | 105 | 140 | - |
| Butadiene, styrene, propylene, polyolefin, adipic acid | 1.30 | 5630 | 1230 | 225 |
| Butadiene, alkylate, methylethyl ketone, styrene, maleic anhydride | 2.0 | 1870 | - | 10 |
| Butadiene, maleic acid, fumaric acid, tetrahydrophthalic anhydride | 3.605 | 959 | 1525 | - |
| Diphenol carbonate, 2-nitro-phenol, benzene, quinolin, $H_2SO_4$, tear gas, dinitro benzoic acid | 0.098 | 650 | 1380 | - |
| Organo-phosphates, esters, resins, phosphorous chlorides | 1.2 | 845 | 2040 | 322 |
| Phenols | 3.215 | 6600 | 13,230 | - |
| 530 different products | 3.2 | 360 | 500 | 673 |
| Organic & inorganic chemicals | 2.1 | 100 | - | - |
| Phenols | 3.72 | 6600 | 13,200 | - |
| Additives for lubricating oils | 0.20 | 465 | 1050 | 250 |
| Polyethylene, ethylene oxide, ethand polypropylene | 2.1 | 385 | 2842 | - |
| Acrylates, insecticides, enzymes, formaldehydes, amines | 1.06 | 1960 | 2665 | 80 |
| Ethylene, propylene, butadiene, crude benzene, toluene | 3.228 | 500 | - | - |
| Acids, formaldehyde, acetone, methanol, ketones, nitric acid, nylon salt, vinyl acetate acetaldehyde | 3.46 | 530 | 10,130 | 160 |
| Isocyanates, polyols, urethane foam | 0.57 | 421 | 1230 | 50 |
| Acetaldehyde | 1.15 | 20,000 | 50,300 | 200 |
| Acrylonitrile, phenol, butadiene | 1.817 | - | 29,100 | - |
| ethylene, propylene, toluene, xylene | 0.41 | 1300 | 1500 | - |
| Acids, formaldehyde, acetone, methanol, ketones, alcohols, acetaldehyde | 1.15 | 15,000 | 30,000 | - |
| Petrochemicals | 15.7 | 177 | - | - |
| Acrylonitrile, Butadiene, styrene, impact polystyrene, crystal polystyrene | [illegible] | 200 | - | 61 |
| Ethylene, propylene, Butadiene alpha-olefins, polyethylenes | [illegible] | 155 | [illegible] | [illegible] |
| Organic chemicals | [illegible] | [illegible] | [illegible] | [illegible] |
| Pharmaceuticals [illegible] | [illegible] | 14,000 | - | [illegible] |
| Organic chemicals | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | [illegible] |
| [illegible] | [illegible] | - | [illegible] | [illegible] |
| Organic chemicals | [illegible] | - | [illegible] | [illegible] |
| [illegible] | [illegible] | - | [illegible] | [illegible] |
| [illegible] | [illegible] | - | [illegible] | [illegible] |
| [illegible] | [illegible] | - | [illegible] | [illegible] |
| [illegible] | [illegible] | - | [illegible] | [illegible] |
| [illegible] | [illegible] | [illegible] | [illegible] | |

## TABLE 12

### EVALUATION OF COD AND BOD WITH RESPECT TO THEORETICAL OXYGEN DEMAND - TEST ORGANIC CHEMICALS

| Chemical Group | (mg/mg) | Measured COD (mg/mg) | COD (%) | Measured $BOD_5$ (mg/mg) | $BOD_5$ (%) |
|---|---|---|---|---|---|
| ALIPHATICS | | | | | |
| Methanol | 1.50 | 1.05 | 70 | 1.12 | 75 |
| Ethanol | 2.08 | 2.11 | 100 | 1.58 | 76 |
| Ethylene glycol | 1.26 | 1.21 | 96 | 0.36 | 29 |
| Isopropanol | 2.39 | 2.12 | 89 | 0.16 | 7 |
| Maleic acid | 0.83 | 0.80 | 96 | 0.64 | 77 |
| Acetone | 2.20 | 2.07 | 94 | 0.81 | 37 |
| Methyl ethyl ketone | 2.44 | 2.20 | 90 | 1.81 | 74 |
| Ethyl acetate | 1.82 | 1.54 | 85 | 1.24 | 68 |
| Oxalic acid | 0.18 | 0.18 | 100 | 0.16 | 89 |
| | Group Average | | 91 | | 56 |
| AROMATICS | | | | | |
| Toluene | 3.13 | 1.41 | 45 | 0.86 | 28 |
| Benzaldehyde | 2.42 | 1.98 | 80 | 1.62 | 67 |
| Benzoic acid | 1.96 | 1.95 | 100 | 1.45 | 74 |
| Hydroquinone | 1.89 | 1.83 | 100 | 1.00 | 53 |
| o - Cresol | 2.52 | 2.38 | 95 | 1.76 | 70 |
| | Group Average | | 84 | | 58 |
| NITROGENOUS ORGANICS | | | | | |
| Monoethanolamine | 2.49 | 1.27 | 51 | 0.83 | 34 |
| Acrylonitrile | 3.17 | 1.39 | 44 | nil | 0 |
| Aniline | 3.18 | 2.34 | 74 | 1.42 | 44 |
| | Group Average | | 58 | | 26 |
| REFRACTORY | | | | | |
| Tertiary - butanol | 2.59 | 2.18 | 84 | 0 | 0 |
| Diethylene glycol | 1.51 | 1.06 | 70 | 0.15 | 10 |
| Pyridine | 3.13 | 0.05 | 2 | 0.06 | 2 |
| | Group Average | | 52 | | 4 |

to 5.33 for methane. Higher ratio values indicate the presence of inroganic-reducing agents. Reported BOD, COD, and TOC values for several chemical and refinery wastewaters are listed in Table 13, the COD/TOC ratio varying from 2.19 to 6.65 (Eckenfelder and Ford, 1970).

The variability between the calculated and measured COD/TOC values for selected organic compounds is shown in Table 14. This variability is attributed to the COD yield, and waste streams containing a portion of these substances would be subjected to a fluctuating COD/TOC ratio in the event of relative concentration changes. The greater the variability in the characteristics of an industrial waste stream, the more pronounced will be the change in its COD/TOC ratio. This in itself is a good indicator of the degree of consistency of wastewater constituents and can be a valuable aid in predicting the design organic load applied to a biological treatment facility.

### COD/TOD Relationship

The COD and TOD values have been correlated for several waste streams, although extensive correlation data from refinery and petrochemical streams is not presently available. The TOD concentration usually can be expected to be higher than the corresponding COD values by virtue of the fact that chemical oxidation is less efficient than that obtained in the catalyzed combustion chamber of the TOD analyzer. Results of TOD analyses for a number of different compounds, for example, indicated that the measured total oxygen demand was usually closer to the theoretical demand values than those obtained using chemical methods (Goldstein, 1968). Preliminary unpublished data indicate that the COD yield of refinery wastewaters ranges from 70 to 84 percent of the total oxygen demand. Unusually high COD/TOD ratios would indicate either that most of the organics oxidized in the TOD analyzer are susceptible to chemical oxidation or that conditions favor the chemical oxidation of inorganics over their oxidation in a catalytic combustion chamber. If the COD/TOD value was unusually low, then the presence of constituents resistant to chemical oxidation would be inferred, or perhaps a more complete oxidation of inorganics in the combustion tube was observed than that obtained chemically. Reported COD/TOD values for untreated industrial wastewaters are tabulated in Table 15 (Ford, Eller and Gloyna, 1970; Wood, Perry and Hitchcock, 1970). These data indicate that average COD/TOD values for the raw industrial wastewaters cited approximate unity, with the variation being attributed to factors previously mentioned.

### Correlation with Chemical and Refinery Data

Recent studies have provided BOD, COD, and TOC data for chemical and refinery process wastewaters discharged from

## TABLE 13

## INDUSTRIAL WASTE OXYGEN DEMAND AND ORGANIC CARBON

| Type of Waste | $BOD_5$ (mg/1) | COD (mg/1) | TOC (mg/1) | BOD/TOC | COD/TOC |
|---|---|---|---|---|---|
| Chemical* | - | 4,260 | 640 | - | 6.65 |
| Chemical* | - | 2,440 | 370 | - | 6.60 |
| Chemical* | - | 2,690 | 420 | - | 6.40 |
| Refinery | - | 226 | 45 | 1.30 | 5.00 |
| Refinery | - | 257 | 51 | 1.20 | 5.00 |
| Chemical | - | 576 | 122 | - | 4.72 |
| Chemical | 24,000 | 41,300 | 9,500 | 2.53 | 4.35 |
| Chemical-Refinery | - | 580 | 160 | - | 3.62 |
| Petrochemical | - | 3,340 | 900 | - | 3.32 |
| Chemical | 850 | 1,900 | 580 | 1.47 | 3.28 |
| Chemical | 700 | 1,400 | 450 | 1.55 | 3.12 |
| Chemical | 8,000 | 17,500 | 5,800 | 1.38 | 3.02 |
| Chemical | 60,700 | 78,000 | 26,000 | 2.34 | 3.00 |
| Chemical | 62,000 | 143,000 | 48,140 | 1.28 | 2.96 |
| Chemical | - | 165,000 | 58,000 | - | 2.84 |
| Chemical | 9,700 | 15,000 | 5,500 | 1.76 | 2.72 |
| Petrochemical | - | - | - | - | 2.70 |
| Olefin Processing | - | - | 133 | - | 2.40 |
| Butadiene Processing | - | 359 | 156 | - | 2.30 |
| Chemical | - | 350,000 | 160,000 | - | 2.19 |

* High Concentration of Sulfides and Thiosulfates

## TABLE 14

## COD/TOC RELATIONSHIPS

| Substance | COD/TOC (Calculated) | COD/TOC (Measured) |
|---|---|---|
| Acetone | 3.56 | 2.44 |
| Ethanol | 4.00 | 3.35 |
| Phenol | 3.12 | 2.96 |
| Benzene | 3.34 | 0.84 |
| Pyridine | 3.33 | nil |
| Salicylic Acid | 2.86 | 2.83 |
| Methanol | 4.00 | 3.89 |
| Benzoic Acid | 2.86 | 2.90 |
| Sucrose | 2.67 | 2.44 |

## TABLE 15

## COD/TOD RATIOS FOR UNTREATED INDUSTRIAL WASTEWATERS

| Type of Wastewater | COD/TOD |
|---|---|
| Refinery Waste | 0.99 |
| Pesticide Manufacturing Waste | 0.95 |
| Petrochemical Waste | 0.98 |
| Petrochemical Waste | 1.20 |
| Petrochemical Waste | 1.12 |
| Plastics Manufacturing Waste | 1.25 |
| Cyrogenics Plant Waste | 1.04 |
| Refinery Waste | 0.71 |
| Combined Refinery-Petrochemical Waste | 0.75 |

various plants (Ford, Eller, and Gloyna, 1970). These analyses were performed daily for a period of several months. The mean values of the array of organic parameters for each industry are plotted in Figure 12, and suggest a general correlation within the concentration limits as shown.

Assuming a linear relationship does exist, variances from the regression line can be attributed to two sources, namely: diversity in wastewater constituents and analytical error. The analytical error is less significant when the dissolved organics are concentrated and highly variable and one would consequently expect the best correlation. However, a diversity in wastewater constituents resulting from in-plant process changes or batch-type operations generally would adversely affect the degree of fit or correlation coefficient. The average organic ratio values observed within each industry and the 95 percent confidence limits are tabulated in Table 16. These data reflect the statistical variations of the parametric ratios only and not the absolute values of the individual BOD, COD, and TOC analyses.

Additionally, the coefficient of variance and the correlation coefficient for the array of parametric ratios observed within each industry is cited in Table 16. The correlation coefficient, which is a measure of the linear covariation of the variables, was used to establish the relative linearity of the parametric ratios between industries. The 95 percent confidence limits of these values can be approximated knowing the number of observations and assuming a normal distribution for each organic parameter.

The following conclusions are based on the values cited in Table 16:

1. Based on a knowledge of the wastewater characteristics and production schedule for each of the industries' studies, the probability of developing a useful correlation between the organic parameters is best when the variation in wastewater concentration is high and the product diversity is low. When this is not the case, there may be no useful correlation.

2. The relationship between these parameters is generally linear and can best be characterized by a least square regression line with the degree of fit expressed by the correlation coefficient and 95 percent confidence limits. The direct ratio of these parameters is most applicable when the regression line converges toward the origin. An intercept on either axis would necessitate the ratio being expressed by a linear equation in the form of $Y = mX + b$.

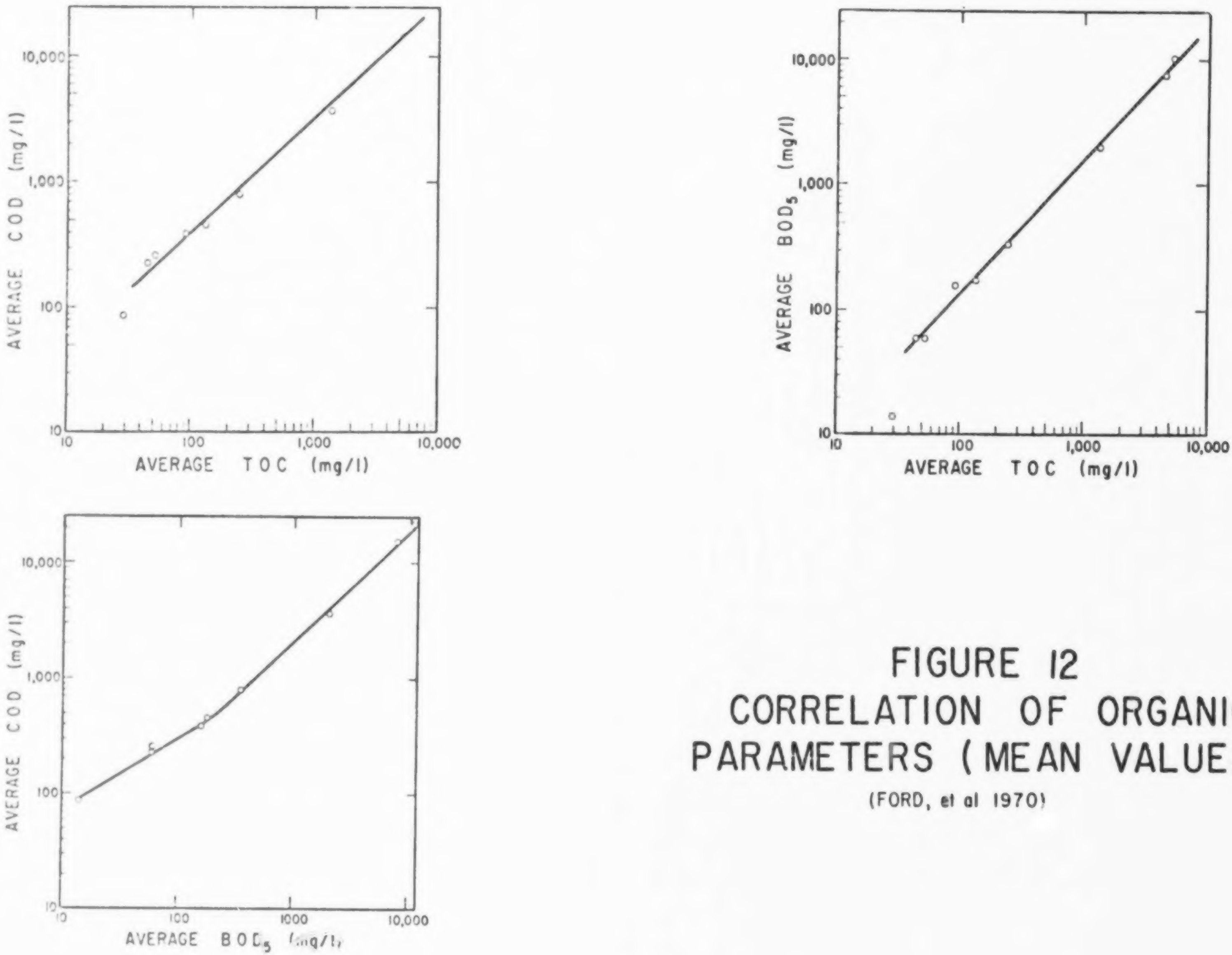


FIGURE 12
CORRELATION OF ORGANIC
PARAMETERS (MEAN VALUES)
(FORD, et al 1970)

## TABLE 16

## STATISTICAL ANALYSIS

| Wastewaters | 95 % CONFIDENCE LIMITS |  |  | Coefficient of Variation |  |  | Correlation Coefficient |  |  |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  | BOD/COD | BOD/TOC | TOC/COD | BOD/COD | BOD/TOC | TOC/COD | BOD/ COD | # OBS | BOD/ TOC | # OBS | TOC/ COD | # OBS. |
| Refinery | 0.31 ± 0.24 | 1.82 ± 0.20 | 0.22 ± 0.18 | 0.39 | 0.05 | 0.41 | 0.38 | 20 | 0.39 | 17 | 0.09 | 34 |
| Refinery | 0.24 ± 0.12 | 1.76 ± 2.20 | 0.18 ± 0.28 | 0.25 | 0.62 | 0.78 | 0.58 | 9 | 0.48 | 7 | 0.41 | 10 |
| Chemical | 0.50 ± 0.30 | 1.59 ± 1.06 | 0.32 ± 0.12 | 0.30 | 0.33 | 0.19 | 0.64 | 16 | 0.51 | 16 | 0.62 | 16 |
| Chemical | 0.39 ± 0.23 | 1.54 ± 0.62 | 0.28 ± 0.12 | 0.29 | 0.20 | 0.21 | 0.49 | 13 | 0.21 | 12 | 0.86 | 13 |
| Chemical | 0.45 ± 0.22 | 1.49 ± 0.68 | 0.31 ± 0.14 | 0.24 | 0.23 | 0.14 | 0.60 | 21 | 0.78 | 20 | 0.50 | 20 |
| Chemical | 0.48 ± 0.36 | 2.08 ± 1.30 | 0.25 ± 0.12 | 0.38 | 0.31 | 0.24 | 0.68 | 20 | 0.90 | 16 | 0.72 | 20 |
| Chemical | 0.56 ± 0.30 | 1.91 ± 1.84 | 0.27 ± 0.16 | 0.27 | 0.48 | 0.30 | 0.97 | 17 | 0.89 | 12 | 0.89 | 12 |
| Chemical | 0.59 ± 0.28 | 1.40 ± 0.44 | 0.41 ± 0.28 | 0.23 | 0.16 | 0.34 | 0.67 | 20 | 0.16 | 18 | 0.34 | 20 |
| Composite | 0.47 ± 0.06 | 1.67 ± 0.38 | 0.28 ± 0.06 | 0.06 | 0.11 | 0.06 | 0.69 | 6 | 0.40 | 5 | 0.72 | 6 |

3. The correlation of COD to TOC was better than BOD to TOC or BOD to COD in most of the cases studied.

Once a correlation of the organic parameters is established for a given wastewater, it should be periodically verified since even a slight process modification or operational change can significantly affect these parametric interrelationships.

Although subject to the aforementioned exceptions, the ultimate BOD of a wastewater is generally assumed to approximate its COD. Therefore, if the observed BOD/COD values of a waste stream are consistently low, i.e., less than 0.3 to 0.5, then the applicability of biological treatment is conjectural. This precept has been confirmed by a series of bench scale simulation studies using biological methods to treat refinery and chemical wastewaters. Representative wastewater samples were pumped to continuous biological reactors, varying the organic loading rate (lbs BOD applied per day per pound mixed liquor volatile suspended solids) in order to determine the optimal loading and dilution requirements. A generalized relationship between the influent BOD/COD ratio and the maximum organic loading allowing 90 percent or better BOD removal was observed. These data are plotted in Figure 13. The one exception to this trend was a wastewater containing a phenolic concentration in excess of 125 mg/1. Although this concentration would be diluted to its sub-inhibitory level in the BOD bottle, the stress of phenolic application inherent with higher organic loadings in this case would exert a deleterious effect on the biological population in the reactor. This would have a net effect of decreasing the BOD removal efficiency in the reactor, illustrating the significance of the presence of inhibitory or toxicological substances as well as their concentration.

Although attempts to use this approach of applying BOD and TOC data were unsuccessful, it is postulated that BOD and TOD data similarly plotted would indicate the same trend.

A different representation of the data is shown in Figure 14, plotting the COD and TOC removal in the biological reactor at a constant organic loading as a function of the influent BOD/COD and BOD/TOC ratios, respectively. It is noted that the COD removal in Figure 14 is greater in all cases than the idealized removal relationship (BOD removal = COD removed). Although this is partially attributable to the $BOD_5$ - $BOD_u$ relationship, it is also indicative of the ability of the microorganisms to better absorb, assimilate, and degrade organic materials in a fluidized biological system than in the BOD bottle, assuming the absence of inhibitory substances in both.

Similarly, the TOC removal in Figure 14 is generally greater than the idealized removal based on the influent $BOD_5$/TOC ratio. The exceptions possibly can be attributed to the fact that either the $BOD_5$ yield of the raw wastewater is abnormally low due to seed

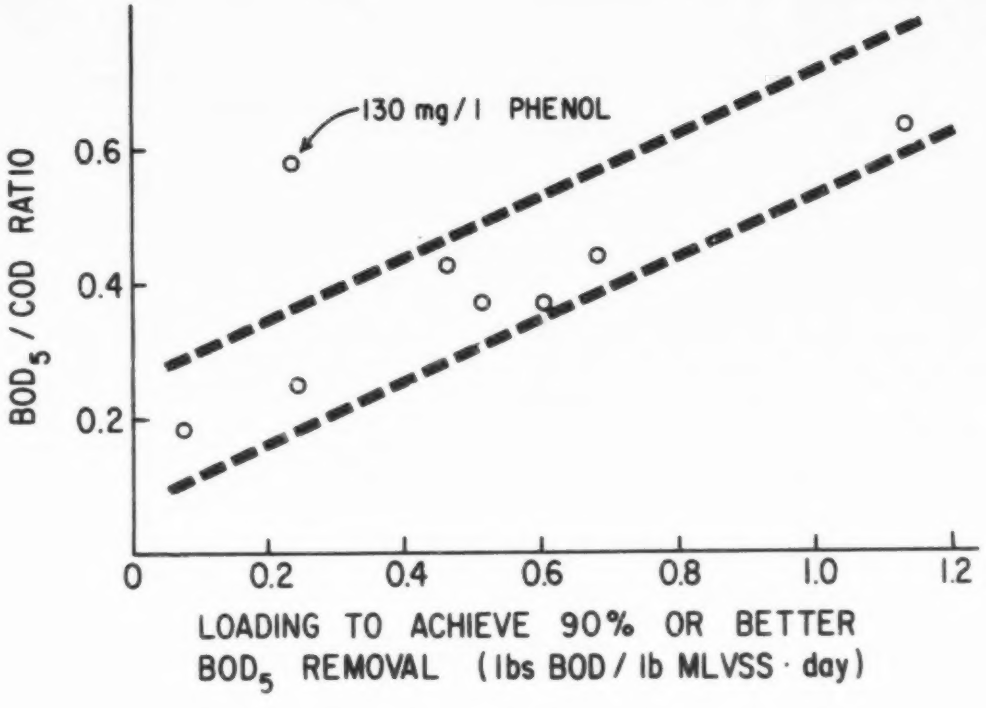
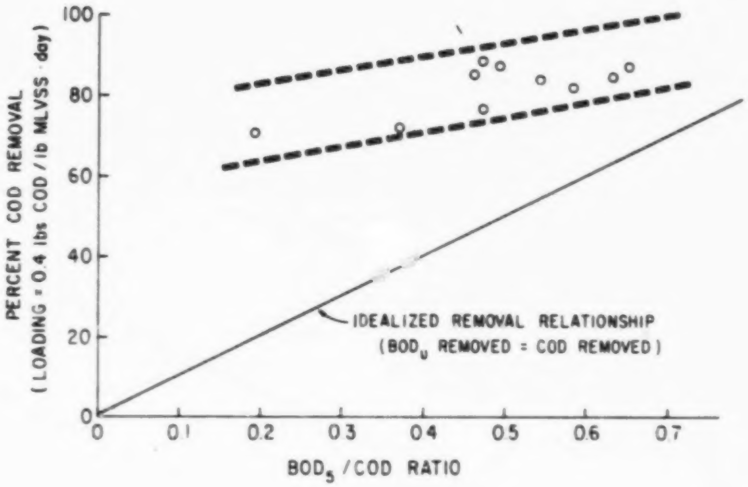


FIGURE 13

EFFECT OF $BOD_5$-COD RATIO ON TREATABILITY

(Ford, et al 1970)



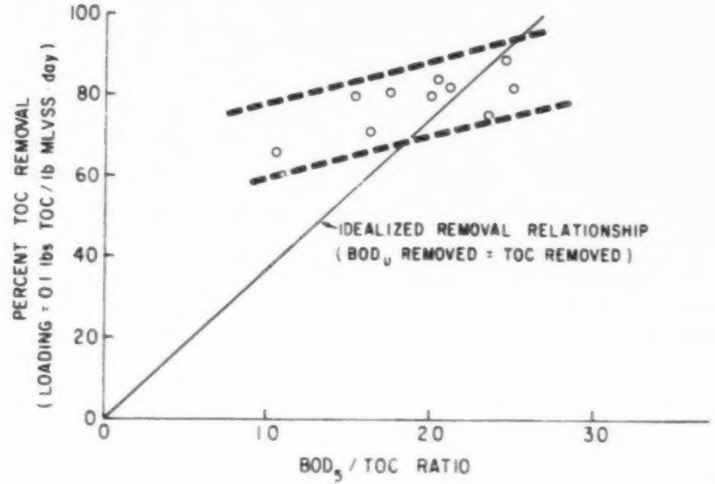


FIGURE 14
EFFECT OF BOD – COD, TOC RATIO ON TREATABILITY

acclimation, environmental factors, etc., or the TOC yield is too high due to the inclusion of inorganic carbon, or both. Additionally, there is the possibility that a substance is inhibitory in the biological reactor but not in the BOD bottle. The dashed lines as shown in Figures 13 and 14 indicate the data groupings and do not represent statistically analyzed limits.

In summary, it can be stated that TOC and TOD are both valid measures of pollution and both can be correlated to COD values in many applications. They are excellent control parameters because of the abbreviated analysis time associated with the analyzers. It is unlikely that COD, TOC, or TOD can be correlated to BOD unless the concentration and nature of constituents in the wastewater remain relatively unchanged. However, the conjunctive use of these parameters in terms of BOD, COD, TOC, and TOD ratios is an effective and logical approach in properly characterizing the organic component of an industrial wastewater.

## Other Organic Parameters

### Oil and Grease

One of the more important parameters applied in characterizing refinery and petrochemical wastewaters is the oil and grease measurement. This is particularly true since oils have both a recovery value and create problems in treatment unit processes. Therefore, oil separation and recovery facilities are required for all oily wastewater streams.

Extraction techniques using various organic solvents, such as n-hexane, petroleum ether, chloroform, and trichloro-trifluoro-ethane are used to evaluate the oil and grease content of wastewaters. The method outlined by the EPA measures hexane extractable matter from wastewaters but excludes hydrocarbons that volatilize at temperatures below 80°C ("FWPCA Methods for Chemical Analysis of Water and Wastes," 1969). Additionally, not all emulsifying oils are measured using these extraction techniques. However, a modified procedure provides for the release of water-soluble oils by saturating the acidified sample with salt followed by isolation on the filter in the accepted manner (Taras and Blum, 1968).

### Phenolic Compounds

Phenols and related compounds are generally prevalent in refinery and petrochemical wastewaters and are of particular significance as they are potentially toxic to marine life, create an oxygen demand in receiving waters, and impart a taste to drinking water with even minute concentrations of their chlorinated derivatives. Primary sources of phenolics are in wastewaters from benzene refining plants, oil refineries, coke plants, chemical operations, and plants which are processing phenols to plastics.

Phenols, or the hydroxy derivatives of benzene, are measured using the distillation approach as per Standard Methods (1965) or by other miscellaneous colorimetric, spectroscopic, or chromatographic techniques (Simard, 1951; Schmauch and Grubb, 1954; Payn, 1960). A rapid, precise, and selective method using ultraviolet differential adsorption also has been recently reported (Martin, 1967).

### Miscellaneous Techniques

There are a multiplicity of other techniques used to identify organic materials in wastewaters other than those previously described. Such techniques are deployed as required to identify specific organics and to monitor their fate through various treatment systems. Gravimetric and volumetric analyses, mass spectrometry, and infrared spectroscopy are classified as the more popular techniques used to characterize refinery and petrochemical wastewaters; while carbon adsorption, liquid-liquid extraction, and gas chromatography often have been used to identify petroleum products in conjunction with pollution-related instances.

## Inorganic Parameters

There are many inorganic parameters which are pertinent when determining potential toxicity, general characterization, or process response. Although the evaluation of any number of inorganic analyses may be required for a particular situation, some of the more prevalent analyses are considered herein (Eckenfelder and Ford, 1970).

### Acidity

The acidity of a wastewater, or its capacity to donate protons, is important because a neutral or near-neutral water is required before biological treatment can be deemed effective, and many regulatory authorities have criteria which establish strick pH limits to final discharges. Acidity is attributable to the unionized portions of weak ionizing acids, hydrolizing salts, and free mineral acids. The latter is probably the most significant as it is difficult to predict neutralization requirements when mineral acidity prevails. Microbial systems may reduce acidity in some instances through biological degradation of organic acids.

### Alkalinity

Alkalinity, or the ability of a wastewater to accept protons, is significant in the same general sense as acidity, although the biological degradation process does offer some buffer capacity by furnishing carbon dioxide as a degradation end-product to the system. It has been estimated that approximately 0.5 pounds of alkalinity (as $CaCO_3$) is neutralized per pound of BOD removed.

### Dissolved Solids

The dissolved solids can have a pronounced deleterious effect on many unit processes included in the waste treatment system. The limiting dissolved salts concentration for effective biological treatment, for example, is approximately 16,000 mg/l. Chloride concentrations of 8,000 to 10,000 mg/l (as $Cl^-$) have also been reported to adversely affect biological systems.

### Ammonia Nitrogen and Sulfides

Ammonia nitrogen is present in many natural waters in relatively low concentrations (100 mg/l), although industrial streams often contain exceedingly high concentrations. The presence of ammonia nitrogen in excess of 1,600 mg/l has proved to be inhibitory to many microorganisms present in a biological aeration basin. Sulfides are present in many wastewaters either as a mixture of $HS^- - H_2S$ (depending on pH), sulfonated organic compounds, or metallic sulfides. Although odors can be caused by the presence of sulfides in concentrations of less than a few hundredths of a mg/l, no inhibitory or biotoxic effects to bacteria are noticed up to concentrations of 100 mg/l (as $S^=$). It should be noted, however, that algal species are adversely affected with sulfide concentrations of 7 to 10 mg/l (Espino and Gloyna, 1967).

### Heavy Metals

The influence of heavy metals on biological unit processes has been the subject of many investigations. Toxic thresholds for Cu, Zn, Cd, etc., have been established at approximately one mg/l, although higher concentrations have been noted to have no effect on process efficiency. For example, zinc concentrations exceeding 10 mg/l had no adverse effect on a biological system creating a petrochemical waste.

Several techniques for heavy metal analysis are given in Standard Methods (1965), although atomic absorption flame photometry is an effective and rapid method for determining small quantities of metals. This method is based on the measurement of a light absorbed at a given wave length by the unexcited atoms of the element being analyzed.

## SUMMARY

From this discussion, it is apparent that the nature and characteristics of the soluble fraction of the wastewater must be evaluated with respect to the unit processes considered. When one speaks of pollution, organic and oxygen-demanding substances are of immediate concern. However, the single or conjunctive use of many parameters, both organic and inorganic, may be necessary to provide the proper analysis of a wastewater.

## IN-PLANT CONSIDERATIONS

The most effective control of wastewaters can be exercised at or near the site of origin. Wastewater control programs are implemented through the use of educational programs for plant personnel, waste elimination during research and development, and installation of waste segregation devices at the source.

Evaluation of in-plant wastewater control measures may be developed in four steps:

1. A wastewater survey, including complete quality characterization and flow measurements,
2. Treatability studies for segregated and combined waste streams, and
3. The recycle or recovery potential of each waste stream based on characterization data and process requirements.

The most effective refinery or petrochemical wastewater collection system incorporates the segregation of waste streams. This may be ideally accomplished by providing separate collection systems for the following streams:

1. "clean" water containing cooling tower and boiler blowdown,
2. highly contaminated process wastes including spills, batch dumps, etc.
3. oily water,
4. non-oily water,
5. contaminated storm runoff,
6. uncontaminated storm runoff
7. sanitary sewers.

The aforementioned categorization of wastewaters permits a rapid assay of potential problems and an evaluation of the effectiveness of in-plant modifications and stream separation. Both refineries and petrochemical plants produce two general types of wastewater: large flows with little contamination; and small, highly contaminated flows. Various uses of raw and reused water in the crude oil refining industry are illustrated in Figure 15. Only about 3 percent of the total water used comes in contact with the product as compared to more than 90 percent that is used for cooling which is less likely to be contaminated.

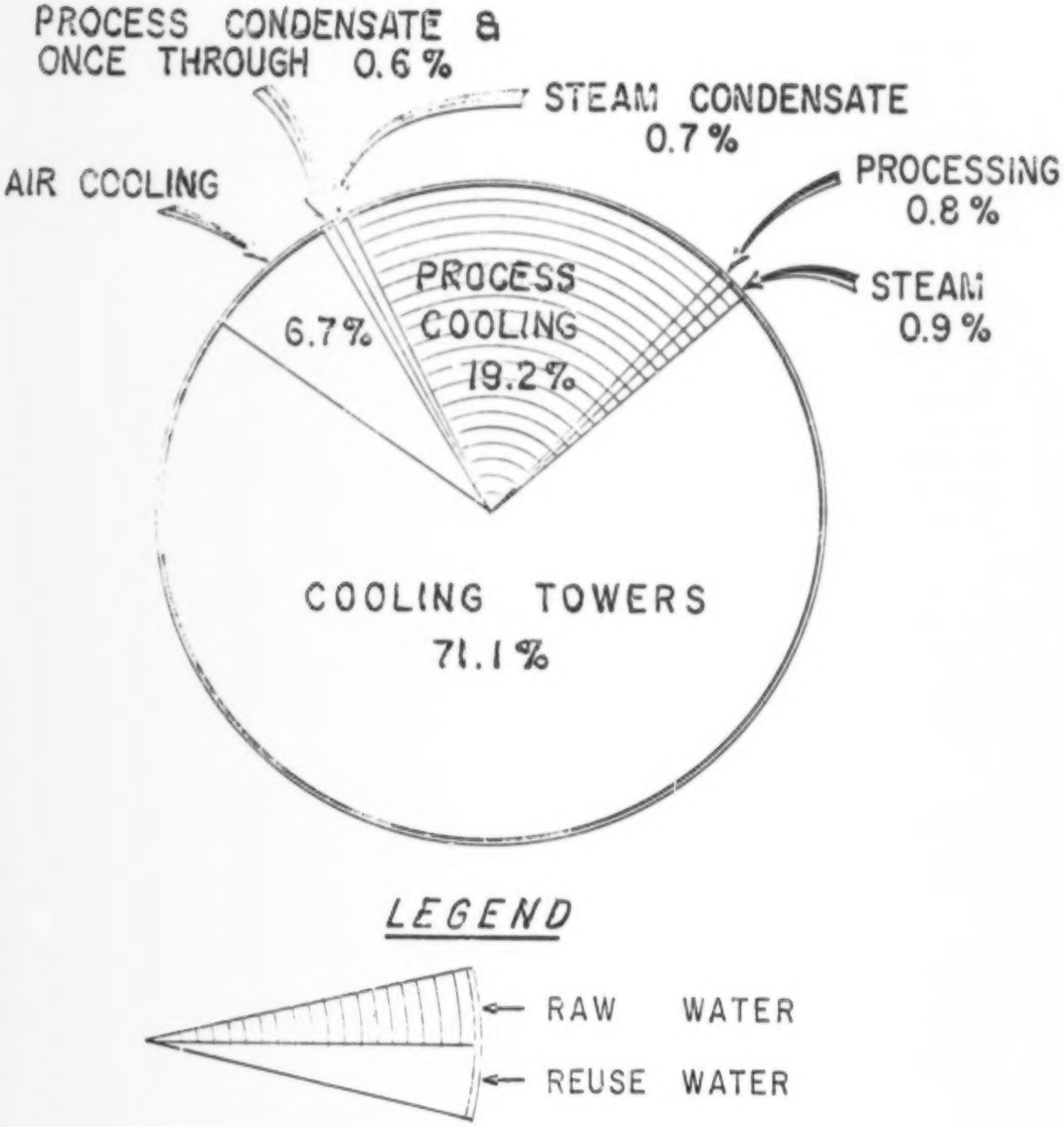


FIGURE 15
TOTAL WATER USE IN REFINERIES
(API, 1968)

## REFINERY WASTE PROBLEMS

Despite the increase of more than 100 percent processing capacity experienced by the petroleum refining industry during the last 20 years (Elkin and Austin 1965), the freshwater requirements and net pollution load per barrel of crude oil processed has steadily decreased. However, refineries have many sources of wastewaters. Problem wastes which are common in almost all petroleum refineries include spent caustic solutions, sulfide waters, phenols, and oils.

### Spent Caustic

Spent caustic solutions from petroleum refineries contain sulfides, mercaptides, sulfates, sulfonates, phenolates, naphthenates, and other organic and inorganic compounds. Methods of treatment include chemical, physical, and biological. Direct disposal into deep wells, thermal incineration, or marketing of wastes has been practiced but the success of these methods has normally been limited to concentrated waste streams.

Chemical treatment methods such as regeneration, air oxidation, and neutralization can be utilized for minimizing spent solution waste discharges. Refinery spent caustic solutions can contain up to 45 percent by volume of acid oils. Separation of acid oils (either phenolic or naphthenic) by neutralization of spent caustic solutions represents one method of treating highly contaminated effluents to a salable end-product.

Reaction water from the springing of phenolic acid oils contains between 10,000 to 15,000 mg/l of dissolved phenolics. Stripping and extraction processes can reduce the phenolics in wastewaters to a level ranging from 100-600 mg/l.

Direct biological treatment of spent solutions is usually not applicable because of high oxygen demand, low pH, and the presence of taste and odor-causing compounds. However, the application of biological treatment methods following extensive pretreatment may be successful, although the economics of such a treatment system should be carefully compared to process alternatives.

### Spent Sulfuric Acid

Extensive use of sulfuric acid as a treating agent and as a catalyst results in acid sludges and acid disposal problems.

Most refineries arrange for their acid suppliers to accept spent sulfuric acid products for recovery or reprocessing. Recovered spent sulfuric acid products, for example, have been used to produce fertilizer grade ammonium sulfate.

## Sulfide Waste Streams

Hydrocracking of feedstocks containing a large percentage of sulfur and nitrogen, typical of Middle East, Venezuelan, and Californian crudes,results in the production of waters containing ammonium sulfide. Extraction and separation of ammonium and hydrogen sulfide from such crudes not only is a necessary process requirement but also results in salable products and decreased water requirements.

## Cooling Tower Blowdown

The greatest quantity of water required in the refining process is used for cooling purposes as shown in Figure 15. Recycle ratios vary between 1 and 30, with the average approximating 3 (Petroleum Industry Refinery Waste Reuse Survey,1968). The quality of cooling water depends upon evaporation and contamination from accidental and intentional additions. This includes the leakage of hydrocarbons from condenser tubes and coolers, chromate or phosphate inhibitor additives, and the accidental commingling of blowdown streams with organic process streams.

## PETROCHEMICAL WASTE PROBLEMS

Because of the diversity of products, it is difficult to generalize regarding the reuse of petrochemical wastewaters. The American Petroleum Institute's Manual on Disposal of Refinery Wastes (1969) summarizes the treatment processes presently used to treat 80 different organic chemicals, 20 inorganic chemicals, and 11 overall plant wastes. Wastewater characteristics associated with some chemical products have been recently summarized (Gloyna and Ford,1969; Rice,1969). All of these chemical waste streams present serious problems whenever the COD exceeds 1,000 mg/l, or when phenols or heavy metals exceed toxic levels. The concentration of various pollutants that interfere with the efficient operation of biological treatment processes has been previously documented (Manual of Refinery Wastes, 1969; Eckenfelder and Ford, 1970). The quality of wastewater from the petrochemical manufacturing processes depends on the type of petroleum feedstock, products manufactured, in-plant control, maintenance, and types of processing equipment.

The major source of low contaminated water in petrochemical industries is the cooling water and steam equipment. The total volume of this water will amount to 10 to 80 percent of the total wastewater and its degree of contamination depends on the following factors:

1. process leaks,
2. water treatment additives,
3. input from air scrubbing, and
4. blowdown and condensates.

These waste streams have a high potential for reuse, but their degree of contamination must be considered.

## By-Product Disposal in Refineries

The present trend towards integration of refineries and petrochemical plants into joint operations located within a single complex may result in minimizing many of the existing wastewater disposal problems. This consolidation is occurring because of the dependency of petrochemical production upon petroleum derivatives, the increasing percentages of chemicals produced at consolidated facilities, and the number of separate refineries that now produce chemicals.

Present trends favor crude oil as a convenient low-cost feedstock for the manufacture of chemicals. It is noteworthy that by-products from chemical manufacturing operations are consumed within the conventional oil refinery framework. These recycles include propylene, butylenes, naptha and gas oil, and gases from the thermal cracking and needle coking operations, non-normal paraffins from the detergent paraffin separation unit, and heavier aromatics from the separation of benzene, toluene, and xylenes.

The ability to consolidate petroleum refining and petrochemical processing in terms of by-product utilization will stimulate growth towards integrated facilities and assist in solving pollution control problems. The potential for continued interest in the concept of integrating chemical industries within refineries is illustrated in Figure 16. The economic ability of a refinery to incorporate chemical production is a function of the size of the base refinery (Beavon, Chute, and Lupfer,1969).

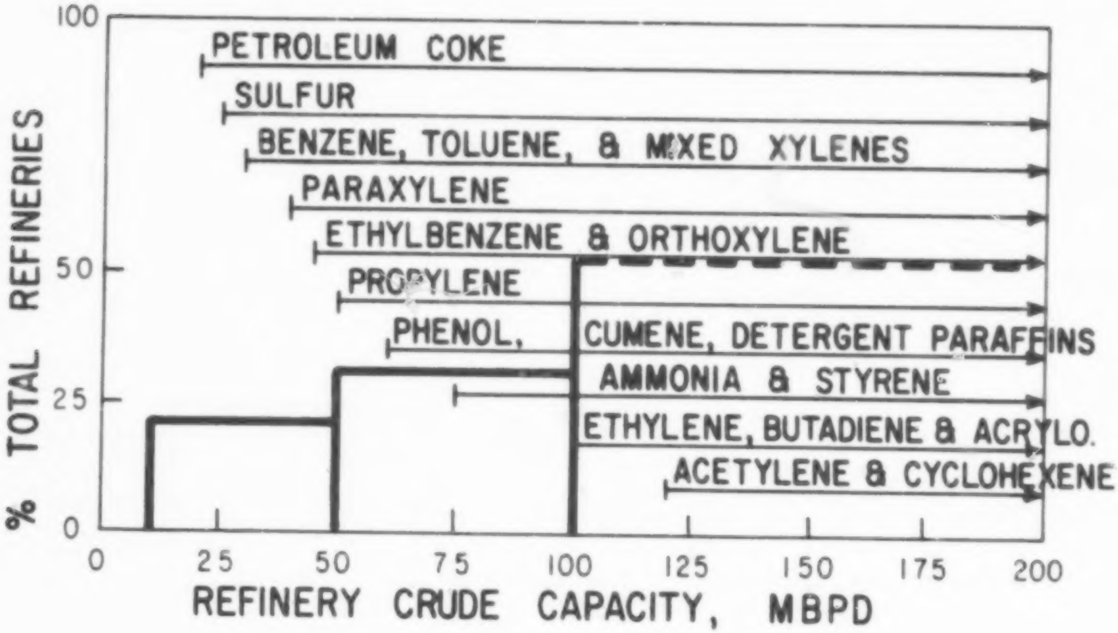


FIGURE 16

MINIMUM REFINERY CAPACITIES FOR
ECONOMIC CHEMICAL MANUFACTURE VERSUS
CAPACITY OF U.S. REFINERIES

Nearly 50 percent of all United States refineries have the capability of economically producing the 10 major petrochemicals. A classification of United States refineries by capacity is also given in Figure 16.

## REUSE POTENTIAL

A recent survey indicates that the refinery industry reuses more of its effluent than any other industry (API,1968). Of the total water used in processing crude oil, only 20 percent is obtained from natural sources. By means of internal cooling, the petroleum industry is reusing 80 percent of the water required for processing each barrel of crude. The trend toward reuse is attributable to economic incentive as well as anti-pollution legislation.

In light of present and forecasted water quality standards, consideration of reusing wastewater should be balanced against the effects of discarding the effluent. When considering economics, the following factors should favor reuse (Koenig,1967):

1. The value of water.
2. Possible pollution damage.
3. The loss of process material.
4. Effluent quality requirements are more stringent than those of the raw water supply.
5. Effluent quality requirements are more stringent than those acceptable for reuse water.

In many areas the costs of treating wastewaters are competitive with freshwater costs. Many factors must be considered before definitive decisions can be made regarding treatment processes and direct disposal. Koenig (1967) made the following general conclusions based on previous cost analysis regarding treatment processes and direct disposal.

### Inorganic Pollutants:

1. Water disposal by spreading at the site is cheaper than any reuse process.
2. For less than 30,000 gal/day, the cost of removing 500 ppm TDS is comparable to injecting to a depth of 12,000 feet or transferring 500 miles by pipeline.

Organic Pollutants:

1. Oxidation ponds are cheaper than any reuse or disposal process including any other means of disposal other than spreading at the site.

2. Coagulation, sedimentation, and filtration costs are comparable to transporting effluent five miles for disposal.

A major consideration where reuse is implemented is the ultimate disposal of the concentrated effluent from a waste treatment unit. For example, waste solutions from ion exchange units will contain more inorganic salts in a smaller volume than did the process water. Complete elimination of all wastewater effluents may result from evaporation using waste heat or product recovery. The advantages of a "closed-loop" or total reuse are significant when considering the costs of treatment and monitoring needed to obtain disposal permits from regulatory agencies.

Another method of effectively eliminating effluents may be possible by establishing a cooperative closed cycle with local government, and in cases where the growth of industry or the establishment of new industry is limited by a freshwater supply, the use of an effluent from a municipal sewage plant may become very favorable. Except for aesthetics, the quality of effluent discharged from properly operated municipal waste treatment facilities is acceptable for many industrial purposes. An arrangement where a municipality accepts and treats an industry's wastewaters and subsequently returns the effluent offers economic incentives and a significant reduction of wastewater discharges.

## ESTABLISHING A REUSE SYSTEM

Complete treatment of refinery effluents by physical, chemical, and biological treatment processes is possible (McPhee and Smith, 1961), although this treatment is usually both expensive and problematic. Nevertheless, water reuse should be incorporated into existing plants and made an integral part of proposed plants.

### Educational Programs

The establishment of educational programs for employees which will inform and describe their role in pollution control can often result in the reduction of the organic pollutants in the final effluent. Opportunities for wastewater reduction through procedural changes, elimination of leakage and spills, and improved housekeeping should be emphasized. Communication programs using plant bulletin boards, articles in the plant paper, and meetings with the personnel involved with particular problems can be effective. Elimination of a pollutant at its source should be emphasized as being more economical and effective than terminal treatment. The effectiveness of an extensive long-term educational program instituted by Union Carbide Corporation is reflected in Figure 17. The 36 percent improvement in effluent quality between 1960 and 1961 in part can be attributed to the inception of an educational program (Rosegarten,1967). The total reduction shown in this Figure resulted from a comprehensive increase in treatment facilities as well as a continuance of employee educational activities. This decrease in pollution was achieved in light of a three-fold increase in plant production.

## Accidental Spill and Drip Prevention

A typical material balance in most refineries would show a three percent loss in crude oil to the sewer (Forbes and Witt, 1965). This loss of product can be partially prevented by the installation of an extensive piping system called a "drip system" (Gloyna, Ford, and Eller, 1969). This system includes the placement of pans under all pumps to catch stuffing box leaks, funnels under all sample cocks to catch drips, and overflow pipes on all vessels to catch lost product. The resulting wastes from these devices are segregated for separate disposal or reinjected into the processing units.

## Segregation and Collection of Runoff

Storm runoff can be a significant source of pollution, depending on the quantity of precepitation and the degree of runoff contact with process products. Effective utilization of dikes to collect spills and rain water, separation of runoff waters, and return of collected runoff waters to process or cooling towers provides a solution to runoff wastewater problems. In order to segregate highly contaminated waters, all process areas should be diked or provided with concrete slabs and curbs. The storage provided in the dike system will depend on the rainfall characteristics and the degree of contamination expected in a given area. In the case of Merichem Company, pumps and dikes were designed to handle as much as a two-inch rainfall of 15 minutes duration (Gloyna, Ford, and Eller,1969). Previous studies had indicated that the first half inch of runoff was highly contaminated, the second half inch was relatively uncontaminated, and the remainder would be of relatively high quality. Based on

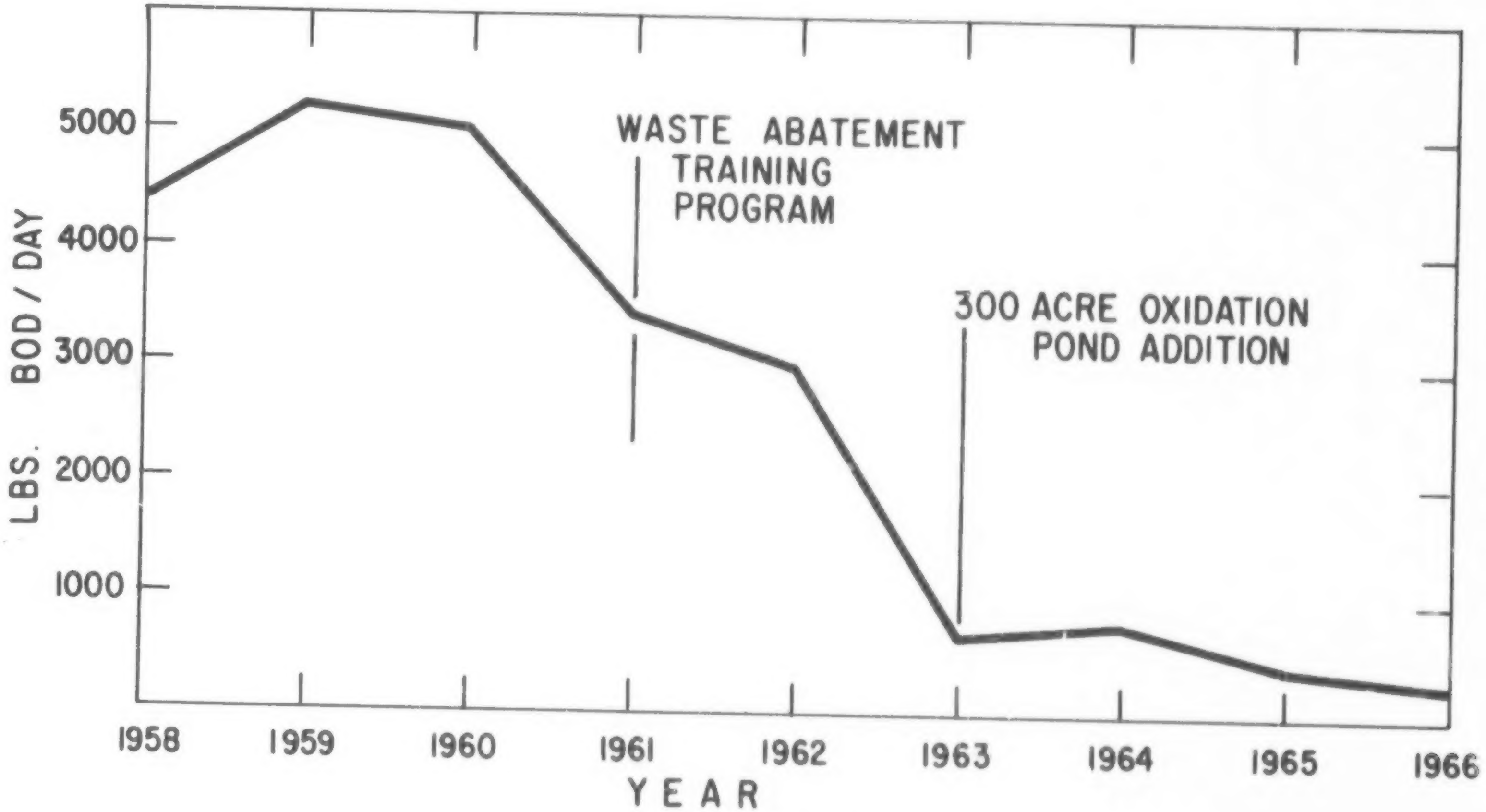


FIGURE 17

AVERAGE DAILY EFFLUENT BOD LOADING. SEADRIFT PLANT UNION CARBIDE, INC.

(Rosengarten, 1969)

these investigations, the first half inch was collected and stored for eventual treatment, the second half inch was used as cooling water makeup, and the excess storm water overflow was determined to be of a quality suitable for release directly to a nearby water course.

## IN-PLANT WATER AND WASTEWATER TREATMENT SYSTEMS

Isolation of potentially highly contaminated wastes identified during the course of the wastewater survey assists in locating product recovery systems or treatment units as well as the implementation of separation operations which may be highly effective in reducing a pollutant source. Examples include sour water strippers or deionizers, direct return of process spills to the process, or use of one waste stream to treat another such as using debutanizer bottoms to extract oils, phenols, and $H_2S$ from quench water processes, spent acids or caustics for neutralization, *etc.*

Another method of reducing the waste load is routing contaminated wastes to the cooling towers, transforming the tower into a treatment unit to remove phenols, $H_2S$, and other organics. The Merichem Company applied this method by returning contaminated storm water to the cooling towers. Organic wastes, heavy metals, and other pollutants are removed by a combination of biodegradation, precipitation, sorption, and volatilization. The amount of sludge buildup in the recycled water is an important consideration since it can interfere with cooling operations by fouling heat exchangers and cooling tower equipment. Merichem's cooling towers, however, operated for over a year while experiencing a minimum of difficulty.

# THE TREATABILITY STUDY

The necessary prerequisite in the formulation of design criteria for industrial wastewater treatment facilities is a treatability study programmed to provide key information relative to the removal of pollutants. The preliminary characterization analyses may be indicative of the types of unit processes applicable in removing various pollutants, but a treatability study is necessary to describe and relate process removal kinetics to the nature and concentration of wastewater contaminants.

There are several approaches which can be employed to evaluate the individual processes which comprise a total waste treatment system. The most obvious technique for process evaluation is to simulate alternate systems on a bench or pilot scale and measure the necessary parameters at various conditions. It should be recognized, however, that the accuracy of information developed from process simulation depends on several factors, vis:

1. The characteristics of the wastewater used in the treatability tests are representative of those anticipated in the field.

2. The physical nature of the bench or pilot scale process is similar to the prototype unit.

3. Independent and dependent operational variables are considered.

4. Environmental parameters affecting process efficiency are defined.

It is apparent from these constraints that the process simulation technique can provide predictor relationships and equations for the treatment process and wastewater in question, but does not necessarily define a specific model with general applications. However, a treatability study which is properly programmed and judiciously implemented does afford the basis for the logical development of unit process selection, design, and predictive performance.

The unit processes considered herein are categorized and tabulated for the purpose of this report according to Table 17 . A general flow and sequence diagram including those unit processes is illustrated in Figure 18 .

Each of the processes cited will be discussed, with bench or pilot scale equipment illustrated as applicable. Although many

## TABLE 17

## CATEGORIZATION OF UNIT PROCESSES

| Process Identification | Unit Process |
|---|---|
| **PRIMARY TREATMENT:** | |
| P-1 | Oil Separation |
| P-2 | Equalization |
| P-3 | Neutralization |
| P-4 | Primary Clarification |
| P-5 | Flotation |
| P-6 | Flocculation-Clarification |
| P-7 | Nutrient Addition |
| **SECONDARY TREATMENT:** | |
| S-1 | Activated Sludge |
| S-2 | Extended Aeration |
| S-3 | Trickling Filter |
| S-4 | Aerated Lagoons |
| S-5 | Waste Stabilization Ponds |
| S-6 | Chemical Oxidation |
| S-7 | Nitrification-Denitrification |
| **TERTIARY TREATMENT:** | |
| T-1 | Chemical Coagulation - Precipitation* |
| T-2 | Gas Stripping* |
| T-3 | Rapid Sand Filtration<br>Microstraining |
| T-4 | Carbon Adsorption |

## TABLE 17 (Cont)

## CATEGORIZATION OF UNIT PROCESSES

| Process Identification | Unit Process |
|---|---|
| **TERTIARY TREATMENT (Cont.):** | |
| T-5 | Electrodialysis* |
| T-6 | Ion Exchange* |
| T-7 | Evaporation |
| T-8 | Reverse Osmosis |
| T-9 | Disinfection by Chlorination |
| **SLUDGE HANDLING AND DISPOSAL:** | |
| SH-1 | Aerobic Digestion |
| SH-2 | Anaerobic Digestion |
| SH-3 | Heat Treatment - Wet Oxidation |
| SH-4 | Thickening |
| SH-5 | Lagooning |
| SH-6 | Sand Drying Beds |
| SH-7 | Vacuum Filtration |
| SH-8 | Centrifugation |
| SH-9 | Filter Press |
| SH-10 | Land Disposal |
| SH-11 | Incineration |
| SH-12 | Sludge Transportation-Sea Disposal |
| **ULTIMATE DISPOSAL:** | |
| UD-1 | Thermal Oxidation |
| UD-2 | Deep Well Disposal |

* May be categorized as primary treatment in certain instances.

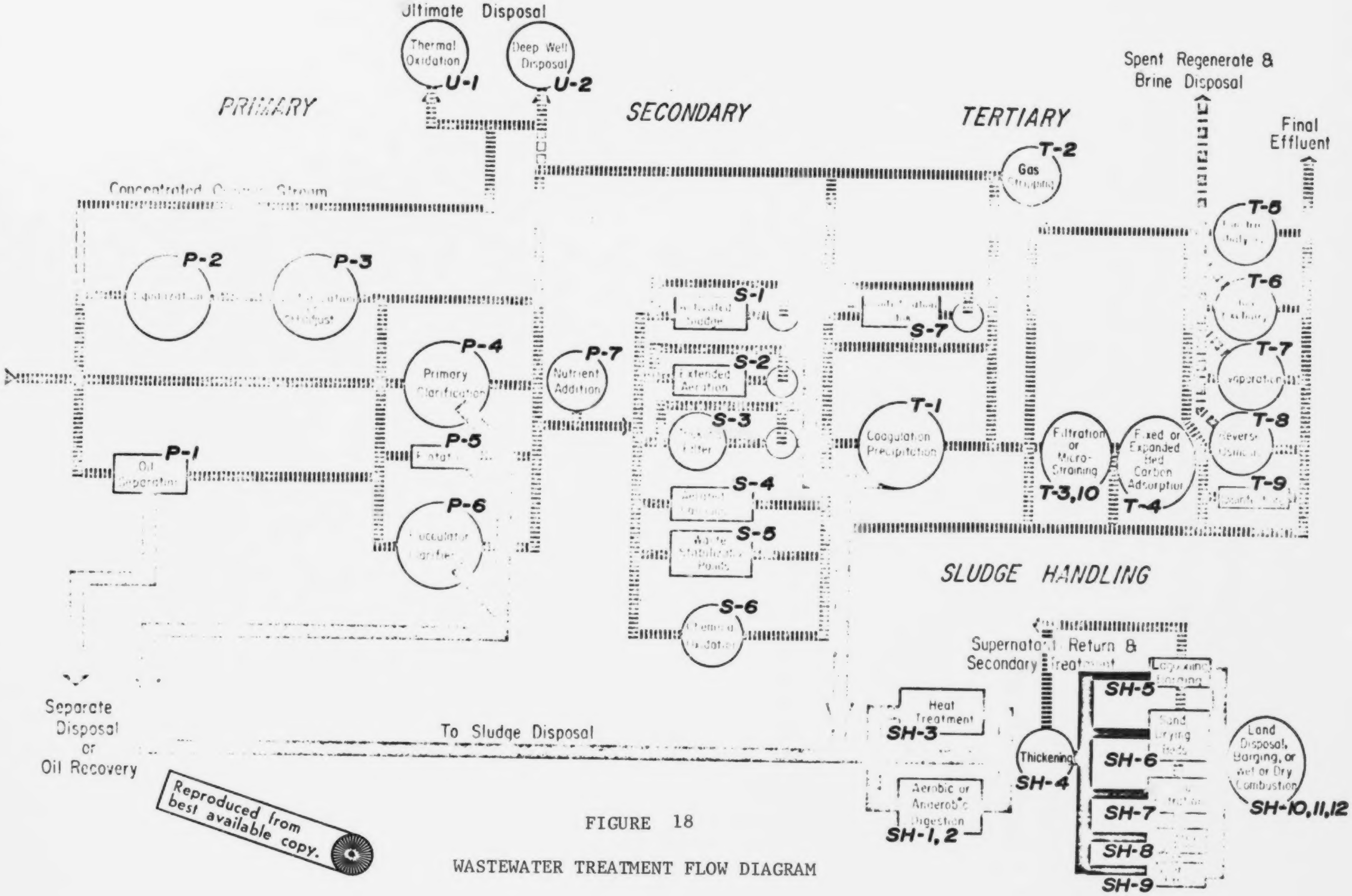

Ultimate Disposal
Thermal Oxidation
U-1
Deep Well Disposal
U-2
PRIMARY
SECONDARY
TERTIARY
Spent Regenerate & Brine Disposal
Final Effluent
Concentrated Stream
T-2
Gas Stripping
P-2
P-3
P-4
Primary Clarification
P-7
Nutrient Addition
P-1
Oil Separation
P-5
P-6
S-1
Activated Sludge
S-2
Extended Aeration
S-3
S-4
S-5
S-6
S-7
T-1
Coagulation Precipitation
Filtration or Micro-Straining
T-3,10
Fixed or Expanded Bed Carbon Adsorption
T-4
T-5
T-6
T-7
T-8
T-9
SLUDGE HANDLING
Supernatant Return & Secondary Treatment
Separate Disposal or Oil Recovery
To Sludge Disposal
Heat Treatment
SH-3
Aerobic or Anaerobic Digestion
SH-1, 2
Thickening
SH-4
SH-5
Sand Drying Beds
SH-6
SH-7
SH-8
SH-9
Land Disposal, Barging, or Wet or Dry Combustion
SH-10,11,12

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FIGURE 18

WASTEWATER TREATMENT FLOW DIAGRAM

of the experimental procedures and design calculations are outlined in detail elsewhere (Eckenfelder and Ford,1970), a general description of these processes within the context of process simulation and treatability is presented herein.

## PRE OR PRIMARY TREATMENT

There are many impurities in petrochemical or refinery wastewaters which must be removed or altered using pre or primary treatment processes before subsequent secondary treatment operations can be considered.

Excessive concentrations of suspended solids discharged directly to secondary biological processes normally decrease overall process efficiency, either by reducing the active biological-solids fraction or by adversely affecting the sludge recycle and wastewater-contact systems. As a consequence, gravity sedimentation or flotation units are used to reduce suspended materials. The removal of suspended or colloidal materials often can be enhanced by applying chemical coagulation in conjunction with sedimentation or flotation.

The removal of oil or grease by gravity separation is required in many instances as these contaminants have a deleterious effect on most secondary and tertiary treatment processes. Since free oils are easier to remove when the concencention is high, oily waste streams generally should flow through gravity separators prior to dilution with non-oily waste streams. Adding chemicals is often required to enhance separation, particularly when emulsions are present.

Extreme acidity or alkalinity must be neutralized before most secondary treatment processes can be properly applied. Although a biological system provides some buffering capacity (by virtue of such mechanisms as biodegradation of organic acids, respiratory carbon dioxide neutralization of caustic alkalinity, etc.), the presence of free mineral acidity or excessive alkalinity in wastewaters dictates a specific neutralization step.

Extreme variations in organic loadings as well as slug discharges of various organic and inorganic constituents can have an adverse effect on the operation and efficiency of primary, secondary, or tertiary treatment processes. Fluctuations in hydraulic loadings have a similar effect. When such conditions are anticipated, equalization and surge facilities are required.

Specific anions such as sulfides or chlorides affect various unit processes in a variety of ways. For example, high chloride concentrations alter biochemical reactions and adversely affect the gravity separation of biological sludges. Toxic or bio-static effects of inorganic constituents such as ammonia or heavy metals or organic compounds such as phenols are well documented and the presence of such materials often necessitates pre or primary treatment steps. Approximate threshold conditions which indicate the need for including pre or primary treatment processes are summarized in Table 18. The pre or primary treatment processes as categorized in Table 17 are listed herein and are described in terms of their treatability or preliminary investigation requirements.

## Oil Separation (Gravity)

### Description of Process

Gravity oil separators are flow-through systems which allow separation of oily substances from the carrier wastewater through a gravity differential. The primary function of the separator is to separate free oil from the wastewater, but it will neither allow separation of soluble substances nor break emulsions (Manual on Disposal of Refinery Wastes, 1969).

In general, oil separators are rectangular, multi-channel structures designed in accordance with the specifications of the American Petroleum Institute (API). Other types of separators which have performed satisfactorily include circular separators, parallel plate separators, and special purpose separators.

### Design Considerations and Process Variables

1. flow
2. rise rate of oil globules in wastewaters
3. turbulence correction factors
4. type and concentration of oil
5. temperature of wastewater
6. viscosity and specific gravity of the wastewater
7. geometry of basin

### Preliminary Investigation Requirements

The feasibility of removing or recovering oils using gravity separators can be estimated using a separatory funnel in accordance with the standard API Procedure 734-53 (Methods for Sampling and Analyses of Refinery Wastes, API, 1969).

TABLE 18

PRE OR PRIMARY TREATMENT REQUIREMENTS

| Constituent | Limiting or Inhibitory Concentration | Treatment |
|---|---|---|
| Suspended Solids | $>125$ mg/l | Lagooning, sedimentation, flotation |
| Oil or Grease | $>50$ mg/l | Skimming tank or separator |
| Heavy Metals | $<$ 1-10 mg/l | Precipitation or ion exchange |
| Alkalinity | 0.5 lbs alkalinity as $CaCO_3$ lb BOD removed | Neutralization for excessive alkalinity |
| Acidity | Free mineral acidity | Neutralization |
| Organic Load Variation | $>$ 4:1 | Equalization |
| Sulfides | $>100$ mg/l | Precipitation or stripping |
| Chlorides | $>$8,000 - 15,000 mg/l | Dilution, deionization |
| Phenols | $>$ 70 - 160 mg/l | Stripping, provide complete mixing |
| Ammonia | $>$ 1,600 mg/l | Dilution; pH adjustment and stripping |
| Dissolved Salts | $>$16,000 mg/l | Dilution, ion exchange |

## Equalization

### Description of Process

Equalization is a method of retaining raw wastewaters in a basin which dampens the fluctuation in its characteristics. The basin should be sized according to the cyclic pattern of the industrial plant operation within practical limits.

If a basin is designed solely to provide for dampening out fluctuations in flow rate, there is no incentive to provide mixing. However, some form of mixing should be provided if wastewater constituents are to be dampened and equalized. This mixing can be provided using proper distribution and baffling techniques, diffused aeration, or mechanical agitation.

### Design Considerations and Process Variables

1. flow variations
2. variations in wastewater constituents
3. cyclic patterns of industrial process operations
4. distribution of wastewaters
5. detention time
6. tank geometry
7. degree and type of mixing

### Preliminary Investigation Requirements

The effect of transient organic or hydraulic loads on a given process operation can be simulated on a bench or pilot scale by varying the feed rates or concentration levels of the wastewater to the unit process in question for defined periods of time. An approach to evaluating the effects of transient loads on biological systems and thereby establishing the criteria for equalization requirements has been recently published (Adams and Eckenfelder,1969).

## Neutralization

### Description of Process

It is not uncommon for petrochemical or refinery wastewaters to contain acidic or alkaline materials which require neutralization prior to subsequent treatment. Neutralization can be accomplished by the use of mixing basins, flow-through beds, or gas sparging.

Acid streams can be neutralized by mixing the waste with lime slurries, dolomitic lime slurries, or by adding caustic soda (NaOH) or soda ash ($Na_2CO_3$). Limestone beds are occasionally used, either as an upflow system or as a downflow system. Alkaline streams can be neutralized with acid (sulfuric, $H_2SO_4$, or hydrochloric, HCl) or with boiler flue gas ($CO_2$). Bottled $CO_2$ is applied to alkaline wastes in a manner similar to that of a diffused air system in an activated sludge plant. It neutralizes alkaline wastes by the same mechanism of flue gas neutralization, *i.e.*, the forming of a weak carbonic acid when dissolved in water.

### Design Considerations and Process Variables

1. alkalinity/acidity
2. quantity of sludge produced
3. flow
4. reaction velocity
5. depth and flow rate (limestone beds)
6. degree of mixing (mixing basins)
7. feed rate of neutralizing agent
8. geometry of mixing basin

### Preliminary Investigation Requirements

The neutralization requirements for a mixing basin system can be estimated in the laboratory by taking samples representative of the alkalinity or acidity level in the wastewater and determining the equivalents per day of neutralizing acid or base required to obtain the desired pH. If limestone beds are to be used, bench scale neutralization columns such as those shown in Figure 19 can be used.

## Primary Clarification

### Description of Process

Sedimentation is a process employed in wastewater treatment to remove solids from suspension. Most suspended materials

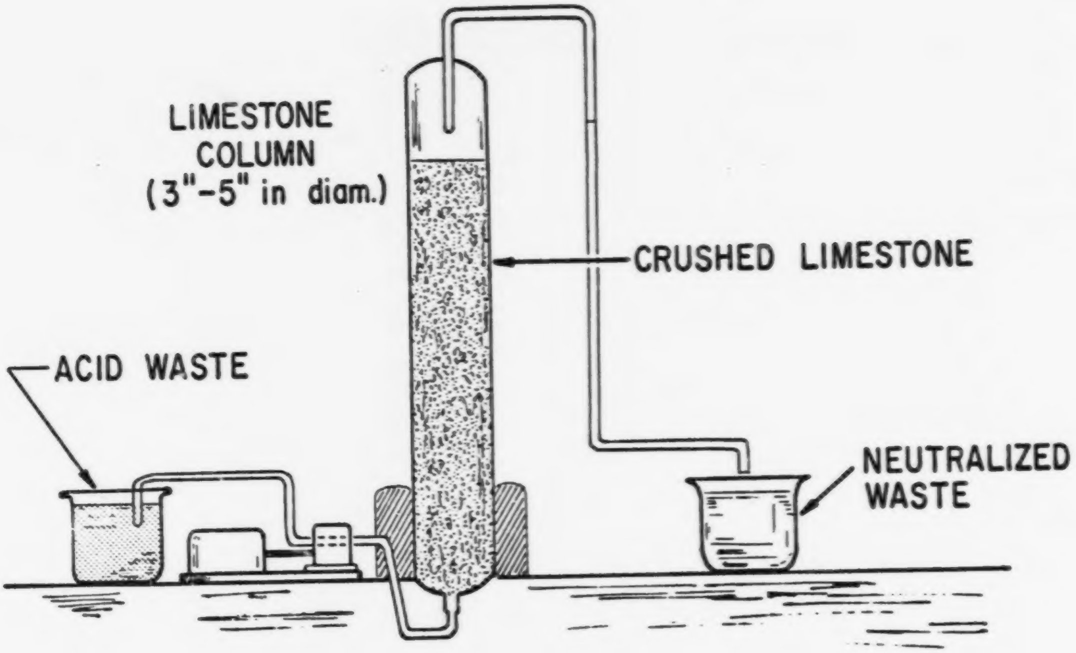
LIMESTONE
COLUMN
(3"-5" in diam.)
CRUSHED LIMESTONE
ACID WASTE
NEUTRALIZED
WASTE

FIGURE 19

BENCH SCALE LIMESTONE COLUMN

in raw petrochemical or refinery wastewaters undergo flocculent settling under quiescent conditions. With this type of settling, particles agglomerate during the settling period with a consequent change in specific gravity and settling velocity.

In the gravity separation of flocculent suspensions, both clarification of the liquid overflow and thickening of the sludge underflow are involved. Sedimentation units are either circular or rectangular and usually have a side water depth of approximately 10 feet.

### Design Considerations and Process Variables

1. flow
2. overflow rate
3. suspended solids concentration in raw wastewater
4. desired underflow concentration
5. settling velocity of suspended solids
6. detention time
7. variation in suspended solids concentration
8. structural & weir configurations of clarification basin
9. sludge raking mechanism and raking speed
10. mechanism of wastewater feed and effluent discharge

### Preliminary Investigation Requirements

The basic design criteria for sizing primary clarification units can be developed using bench scale batch settling tests or pilot scale continuous flow clarifiers. The batch settling cylinder as used in the laboratory is shown in Figure 20. The concentrations of suspended materials are observed at various levels for various settling times, and this data can subsequently be formulated into the design.

## Flotation

### Description of Process

Flotation is a process used to separate the solid phase from the liquid phase, having the same objectives of gravity sedimentation. However, separation of the 2 phases is enhanced by the pressurization of the incoming or recycled wastewater,

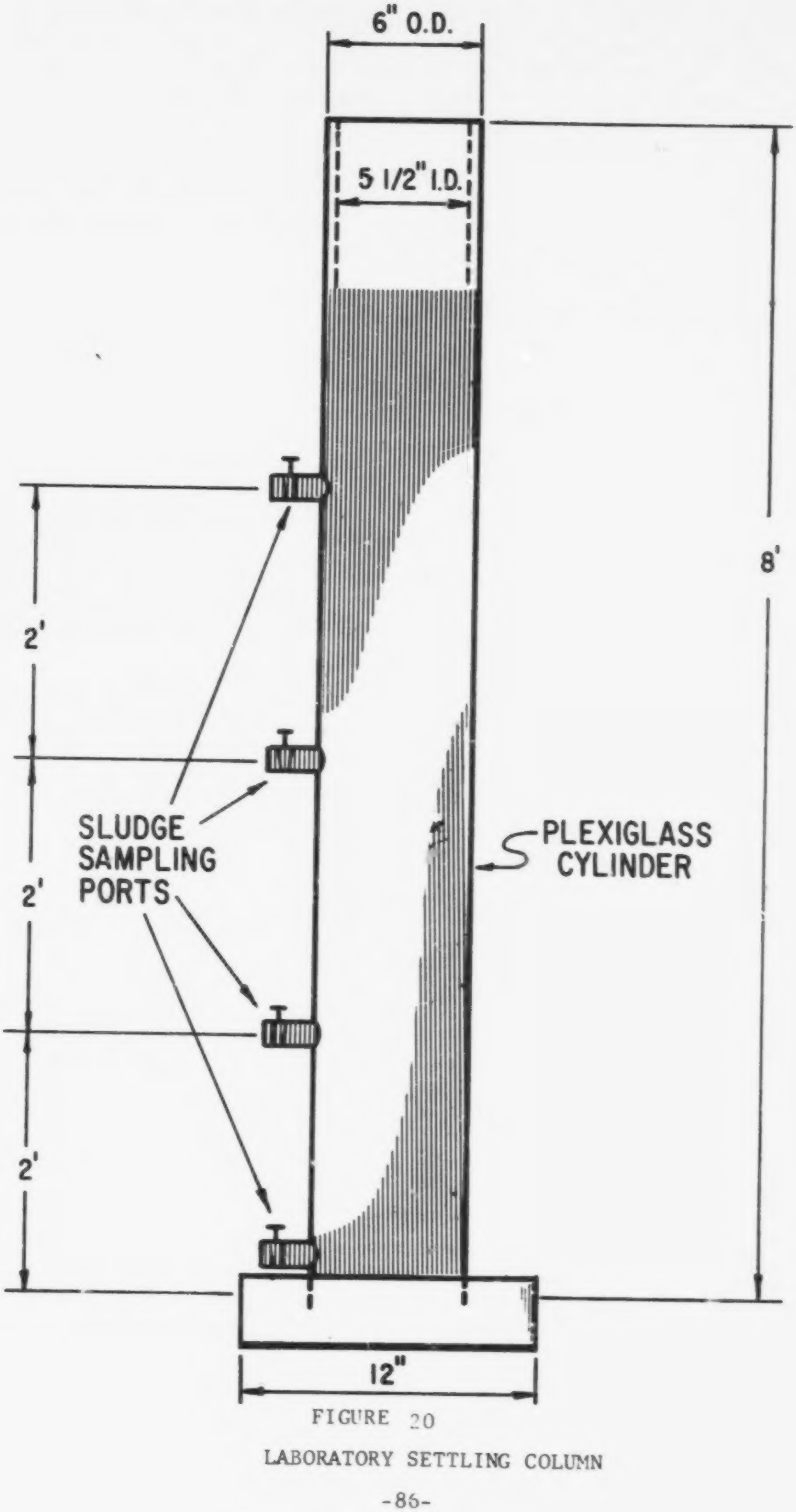
6" O.D.
5 1/2" I.D.
8'
2'
2'
2'
SLUDGE SAMPLING PORTS
PLEXIGLASS CYLINDER
12"

FIGURE 20

LABORATORY SETTLING COLUMN

the release of which provides minute bubbles which attach themselves to or become enmeshed in the suspended particles. The air-solid particles rise to the surface of the flotation unit from which they are removed by a sludge collection mechanism, while the underflow represents the clarifier effluent.

Flotation units are often applicable in removing or reducing the concentration of oily materials present in petrochemical or refinery wastewaters. It is not uncommon to employ gravity separation devices followed in series by flotation units. The efficiency of a flotation unit in removing oil depends on the nature of the oil, its initial concentration, and the level of associated particulate matter. Chemical coagulants are occasionally used to enhance the separation process.

### Design Considerations and Process Variables

1. flow
2. recycle ratio
3. air/solids ratio
4. detention time
5. rise rate
6. overflow rate
7. solids loading

### Preliminary Investigation Requirements

The applicability of the flotation separation of solids from liquids can be determined on a bench or pilot scale. Such an evaluation can be made using the pressurized chamber apparatus shown in Figure 21. The wastewater is pressurized and proportionately mixed with additional water in an open container. The rise rate and concentration of the floated material is then noted and used as a basis for the selection and design of flotation systems.

## Coagulation - Precipitation (Reactor-Clarifiers)

### Description of Process

Reactor-clarifiers are used to combine chemical coagulation-precipitation with gravity sedimentation. These units are particularly applicable when the addition of chemicals significantly enhances the removal of colloidal and suspended materials. Most reactor-clarifiers employ concentric baffles with the center compartment containing chemical feed and mixing appurtenances.

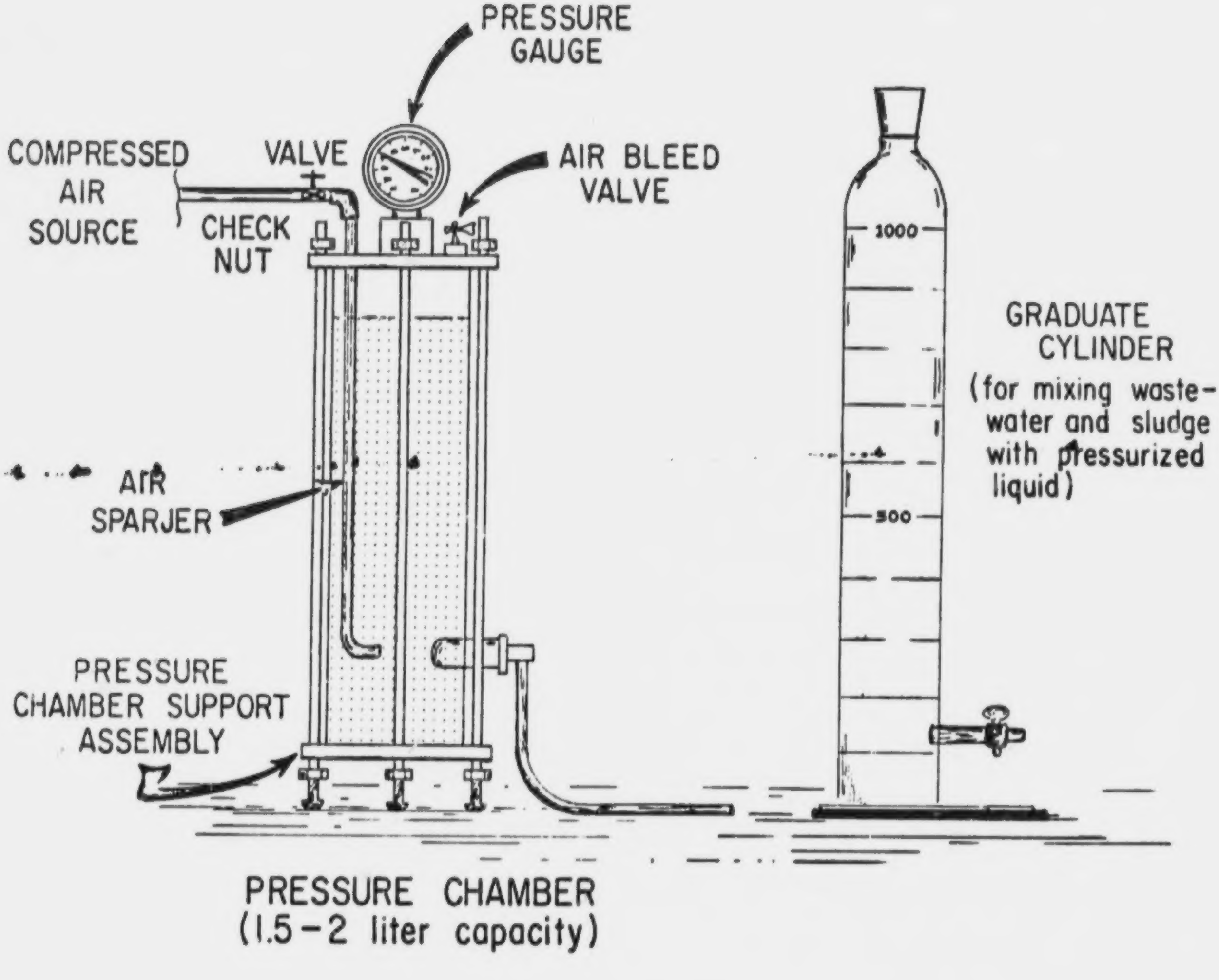
PRESSURE GAUGE
COMPRESSED AIR SOURCE
VALVE
AIR BLEED VALVE
CHECK NUT
1000
GRADUATE CYLINDER
(for mixing wastewater and sludge with pressurized liquid)
AIR SPARJER
500
PRESSURE CHAMBER SUPPORT ASSEMBLY
PRESSURE CHAMBER
(1.5 − 2 liter capacity)

FIGURE 21

BENCH SCALE FLOTATION UNIT

A scraping mechanism is used in the bottom portion of the quiescent zone to allow for collecting and concentrating the resulting sludge.

### Design Considerations and Process Variables

1. flow
2. overflow rate
3. suspended solids concentration in raw wastewater
4. desired underflow concentration
5. effect of various chemical coagulants on settling velocities and underflow concentration
6. dosage of chemical coagulants
7. pH effect on chemical coagulation & precipitation
8. size of reactor compartment and level of mixing
9. sludge raking mechanism and raking speed
10. mechanism of wastewater & chemical feed & effluent discharge

### Preliminary Investigation Requirements

The efficacy of using chemical coagulation-precipitation can be assayed in the laboratory using the standard jar test procedure, varying the pH, coagulant, and coagulant dosage, to determine the conditions for maximum removals of suspended materials or organic constituents. The effectiveness of adding coagulants to a wastewater is normally measured in terms of color removal, organic reduction (such as TOC, BOD, *etc*.), and suspended solids removal.

## Nutrient Addition

### Description of Process

Efficient and successful biological oxidation of organic wastewaters requires a minimal quantity of nitrogen and phosphorus necessary for the synthesis of new cellular tissue. Since many petrochemical and refinery wastewaters are deficient in both constituents, facilities must be provided to supply the wastewater with these critical nutrients (Eckenfelder and O'Connor, 1963).

Nitrogen in the form of anhydrous ammonia, nitrite, nitrate, and some forms of organic nitrogen are available to microorganisms, although it is normally assumed that nitrogen is taken into the cell in the form of ammonia. This means that a reduction of nitrite and nitrate-nitrogen is required before nitrogen is available as a nutrient source. Phosphorus is usually added in the form of phosphoric acid or soluble phosphorus salts since they are the most readily assimilable. It is generally assumed that a BOD/N/P ratio of 100/5/1 is required for proper microbial respiration and reproduction, although an alternate way of calculating the requirement is based on the daily synthesis sludge production; vis,

Nitrogen requirement = 0.123 (sludge production/day)

Phosphorus requirement = 0.026 (sludge production/day)

Nitrogen or phosphorus storage tanks are located in the proximity of the raw wastewater influent to secondary biological treatment facilities.

### Design Considerations and Process Variables

1. organic load in terms of BOD
2. nutrient feed rates
3. mixing of applied nutrients with incoming wastewater
4. form of nitrogen and phosphorus and level of purity
5. levels of nitrogen and phosphorus in wastewater

### Preliminary Investigation Requirements

The effect of nutrients on biological systems can be evaluated on a bench or pilot scale by measuring the organic removal obtained in biological facilities with varying concentrations of nutrients added.

## SECONDARY TREATMENT

Secondary treatment is applied to reduce dissolved organic constituents through chemical or biochemical oxidation to a level acceptable for discharge into a receiving body of water or to the point where tertiary treatment can be effectively employed. Biological systems are the most common processes used for secondary treatment, although chemical oxidation, which has a more restrictive application, can be similarly classified. Commonly used biological treatment systems include activated sludge, extended aeration, aerated lagoons, trickling filters, and waste stabilization ponds. The biological transformation and removal of nitrogen through nitrification-denitrification processes is classified for the purpose here as a secondary treatment, although such a system sometimes is categorized as a tertiary process.

Screening analyses often are necessary to distinguish biologically treatable streams from those which are biologically resistant or toxicological. This is partially true in a complex petrochemical facility where a treatability evaluation of major waste streams is required in order to plan the total waste treatment system. Biological screening tests can be conducted using either manometric techniques or bench scale batch reactors (Eckenfelder and Ford, 1970). These screening procedures will be discussed individually.

1. Batch Reactor Screening Analyses

   A series of small batch-type biological reactors as shown in Figure 22 can be used to accomplish the same objectives as the Warburg approach. An acclimated seed is added to each of a series of batch units, then either various concentrations of a single waste stream or wastewater samples from each stream are added at a volume proportioned by flow to each reactor. Results such as those shown in Figure 23 indicate apparent toxicity or inhibition, using COD or BOD removal as a comparative index.

2. Manometric Analyses (Warburg Respirometer)

   The Warburg Respirometer can be used to obtain a cursory estimate of the effect of various waste streams on biological cultures by measuring the biological response in terms of oxygen uptake for different classifications and concentrations of wastewater. This can be accomplished using an approach similar to that described in Manometric Techniques. An acclimated biological seed plus the wastewater sample are added to the manometric flask. As the microorganisms utilize the organic constituents of the wastewater, the corresponding pressure differential in the closed system resulting from oxygen utilization is recorded. Results as shown in Figure 24 indicate the percent by volume of the particular waste stream which is toxic or inhibitory to a biological system (allowance should be made if lag periods of oxygen utilization caused by the incomplete acclimitization of the biological seed occurs).

Chemical oxidation is not economically competitive with biological oxidation for most applications, but it offers several conceptual advantages. It is not overly sensitive to fluctuating environmental conditions, is generally more efficient in the attack on stable or refractory compounds, and can effectively be controlled and regulated.

The secondary treatment processes as tabulated in Table 17 are described in terms of their preliminary investigation requirements.

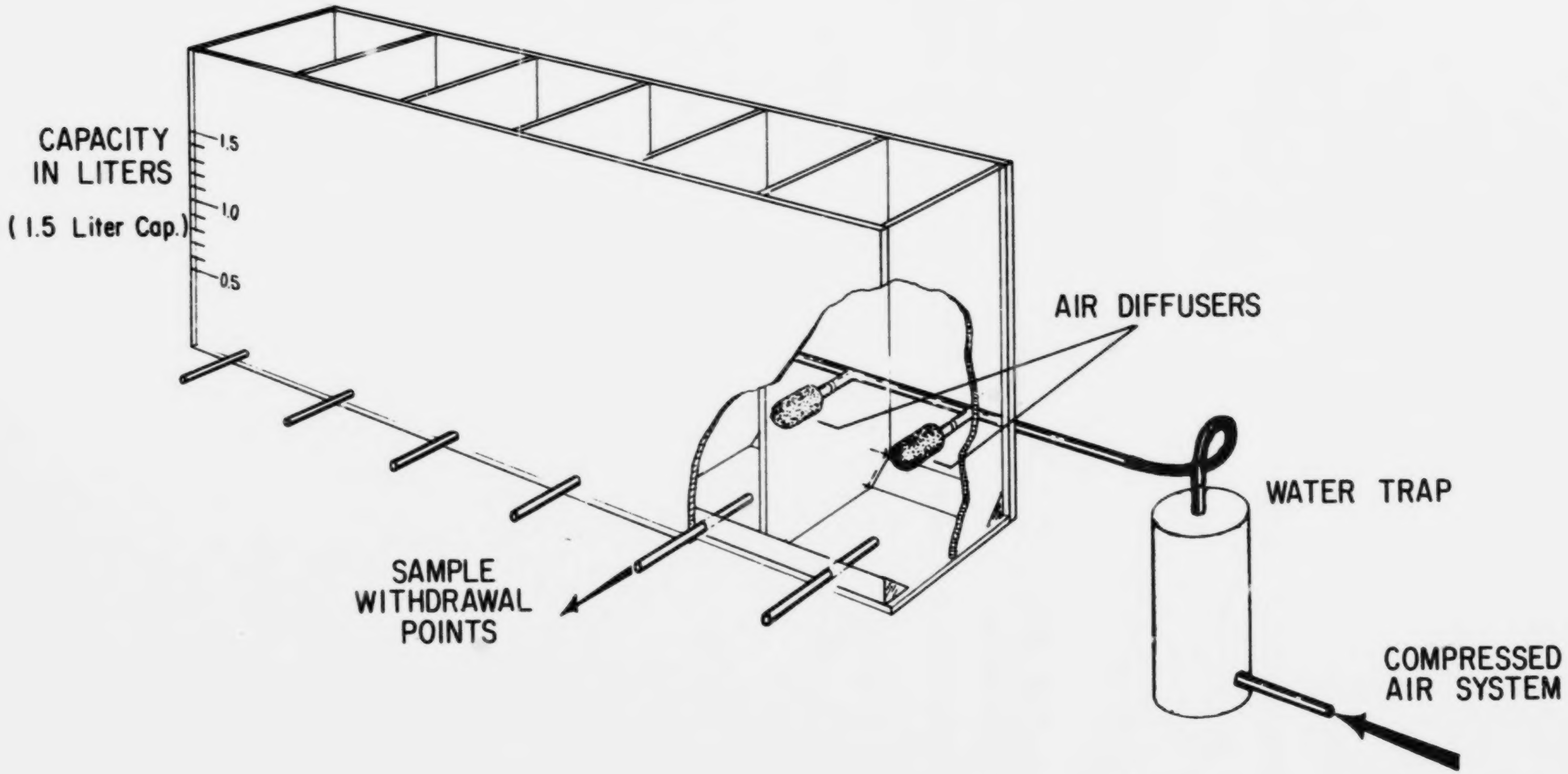
CAPACITY
IN LITERS
( 1.5 Liter Cap.)
1.5
1.0
0.5
AIR DIFFUSERS
WATER TRAP
SAMPLE
WITHDRAWAL
POINTS
COMPRESSED
AIR SYSTEM

FIGURE 22

BATCH REACTOR

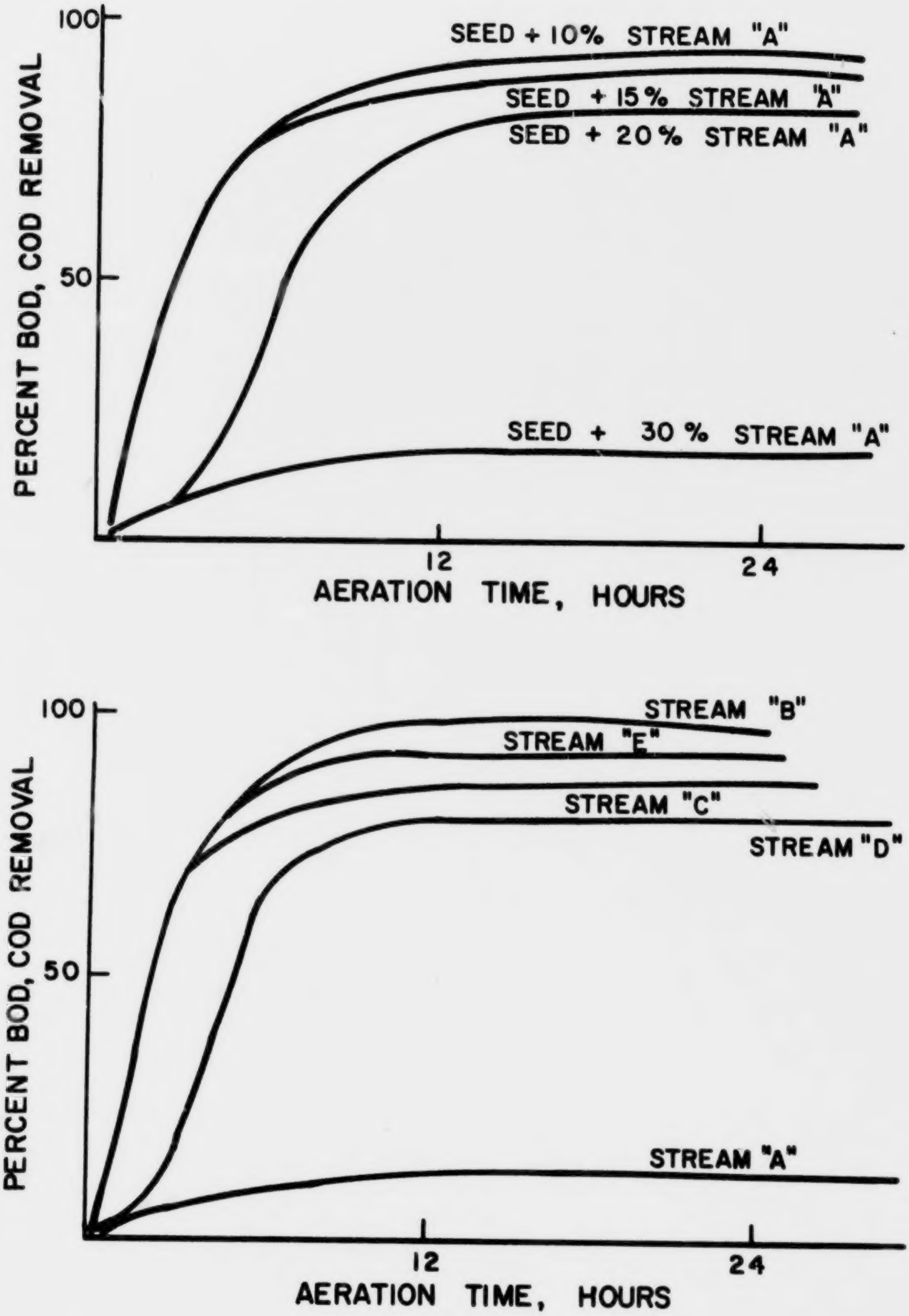

FIGURE 23

SCREENING PROCEDURES USING BATCH BIOLOGICAL REACTORS

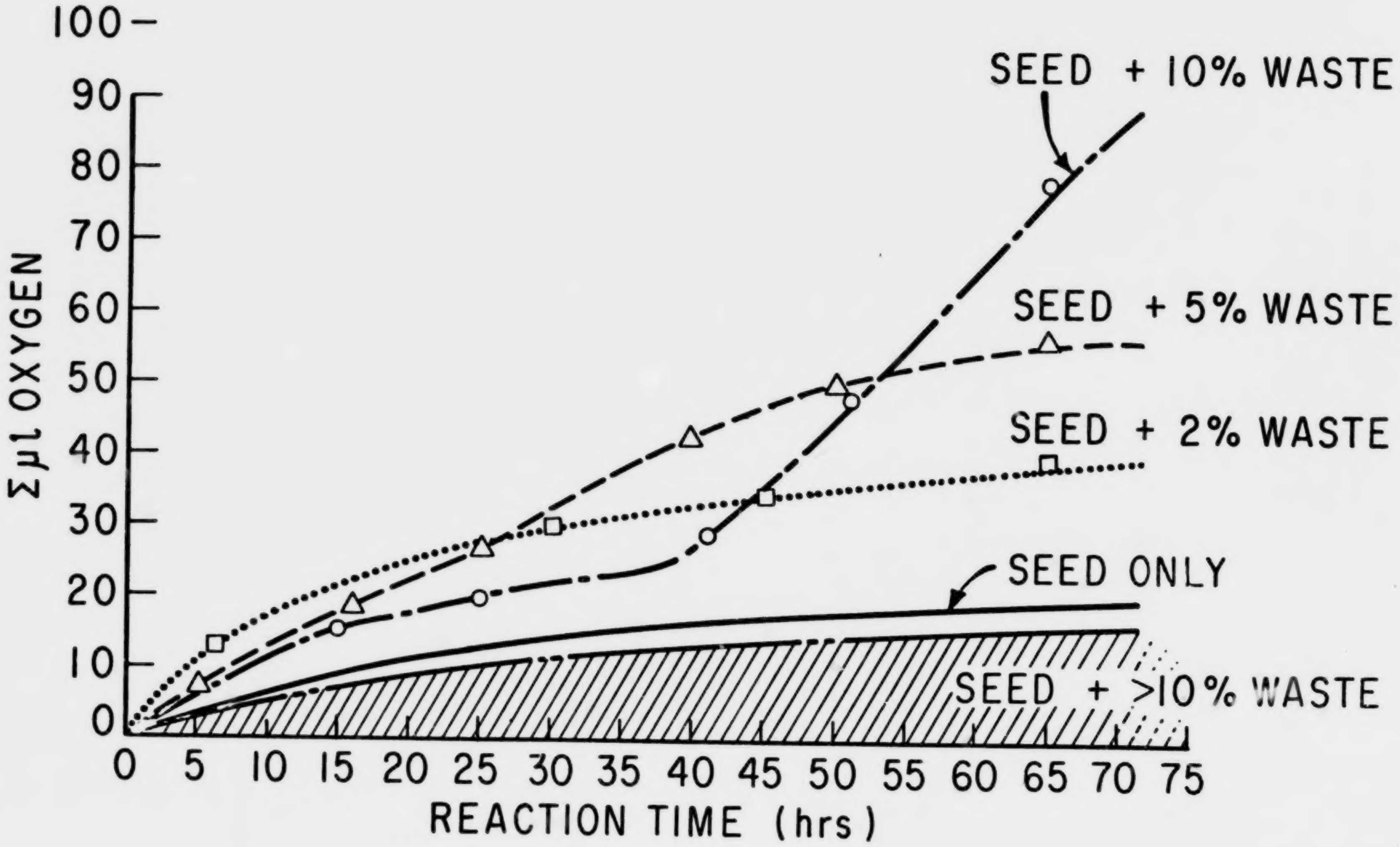

FIGURE 24

DILUTION EFFECT ON RESPIRATION RATES

## Activated Sludge

### Description of Process

The activated sludge process provides an environment in which flocculated biological growths and wastewater are continuously mixed in the presence of dissolved oxygen. The microorganisms remove organic materials from the waste through physical sorption and aerobic biological oxidation. The biological floc suspensions are then separated by settling, recirculating a portion of the thickened sludge to the aeration basin for contact with additional waste. Excessive sludge accumulation must be wasted and subsequently treated. Oxygen and mixing in the aeration basin are provided by diffused or mechanical aeration.

### Design Considerations and Process Variables

1. organic loading
2. environmental factors (pH, temperature, *etc*.)
3. nature of wastewater and fluctuation in characteristics
4. level of mixing in aeration basin
5. geometry of mixing basin
6. nature of sludge
7. nutritional requirements

### Preliminary Investigation Requirements

The activated sludge process can be evaluated in the laboratory using the batch reactors shown in Figure 22 or a continuous flow reactor such as the one shown in Figure 25. Although batch-type studies are acceptable for screening analyses and approximating organic removal rates and effluent levels, bench or pilot scale continuous studies are recommended for the development of design criteria. This is predicated on the following factors:

1. Food/microorganism ratios which dictate process kinetics reach equilibrium values in continuous reactor studies, and this information can be more accurately translated to continuous-flow prototype units. Process kinetics are highly dependent on the time variable in batch reactor studies.

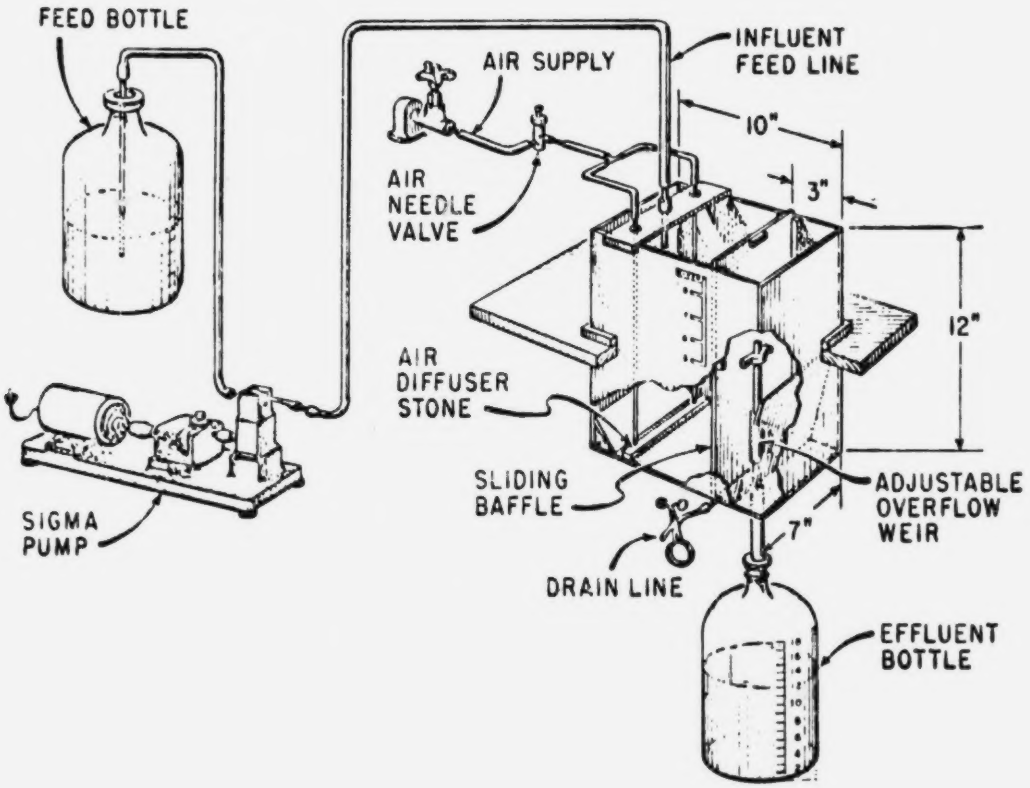
FEED BOTTLE
INFLUENT FEED LINE
AIR SUPPLY
AIR NEEDLE VALVE
10"
3"
12"
AIR DIFFUSER STONE
SLIDING BAFFLE
ADJUSTABLE OVERFLOW WEIR
7"
SIGMA PUMP
DRAIN LINE
EFFLUENT BOTTLE

FIGURE 25

CONTINUOUS FLOW LABORATORY REACTOR

2. Oxygen requirements and sludge growth rates observed in continuous reactors have been shown to approximate those values observed in full-scale units when operating conditions are the same. Predictor data derived from batch data has been more inaccurate, and,

3. The impact of toxic or inhibitory substances, and variation in flow and constituents, on the biological system can be more accurately evaluated for continuous systems when continuous bench or pilot scale reactors are used.

## Extended Aeration

### Process Description

Extended aeration is a modification of the activated sludge process where the organic loading is sufficiently low to allow oxidation of biological solids (endogenous respiration), thus minimizing the excess sludge production attributable to biological synthesis. The sludge is theoretically nonbiodegradable residue but still contains an active biological fraction.

Extended aeration facilities generally are most applicable when the design wastewater flow is less than 2 to 3 MGD because of the tank volume requirements.

### Design Considerations and Process Variables

1. organic loading
2. environmental factors (pH, temperature, *etc*.)
3. nature of wastewater and fluctuations in characteristics
4. level of mixing in aeration basin
5. geometry of mixing basin
6. nature of sludge
7. nutritional requirements

### Preliminary Investigation Requirements

The extended aeration process can be evaluated in a manner similar to that of the activated sludge process. The detention time (or organic loading) required to minimize sludge production can be estimated by evaluating the sludge production per unit time for each of the continuous bench scale reactors subjected to varying organic loadings. The loading at which sludge production is minimized can be considered the point where the system by definition is extended aeration.

## Trickling Filters

### Description of Process

Trickling filters use a biological slime coated on a fixed media bed to remove dissolved and colloidal organic materials as the wastewater flows through. As the wastewater comes into contact with the slime, the organic material and oxygen diffuse into the growths where biochemical oxidative reactions occur.

The characteristics of the media should be such that it provides not only a maximum contact surface area of active biological mass, but also allows maximum wastewater-slime contact time without filter plugging. Good ventilation throughout the filter bed is also required.

### Design Considerations and Process Variables

1. filter depth
2. filter media
3. hydraulic and organic loading
4. wastewater characteristics
5. environmental factors (pH, temperature, *etc.*)
6. recycle pattern
7. nutrient requirements

### Preliminary Investigation Requirements

Trickling filters can be evaluated in the laboratory using a filter model as shown in Figure 26. By varying the hydraulic load, filter depth, and recycle ratio, the parameters necessary for developing the predictor equations can be measured, and the constants which define the substrate removal and filter media can be estimated (Eckenfelder and Ford, 1970).

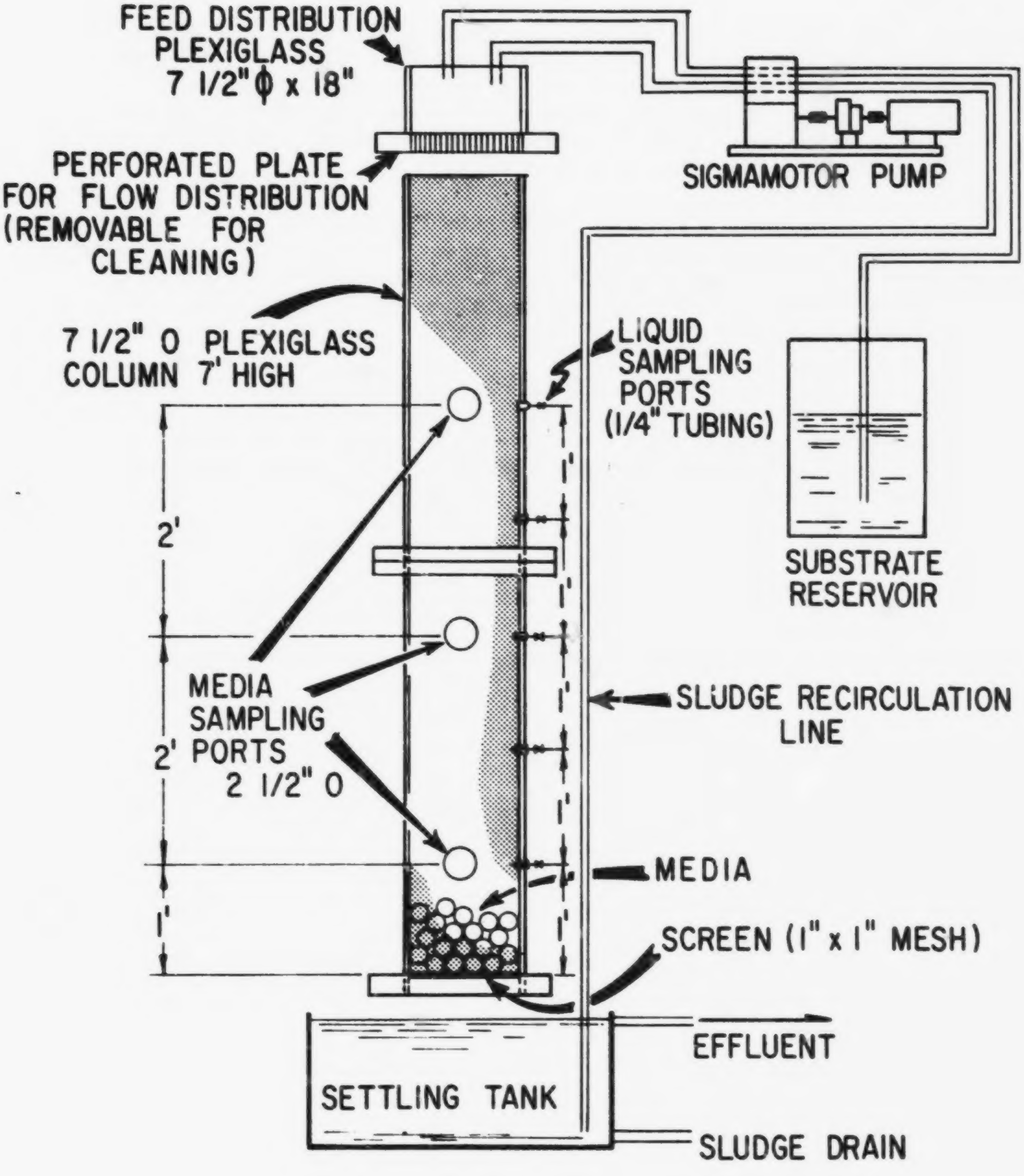
FEED DISTRIBUTION
PLEXIGLASS
7 1/2" ϕ x 18"
PERFORATED PLATE
FOR FLOW DISTRIBUTION
(REMOVABLE FOR
CLEANING)
SIGMAMOTOR PUMP
7 1/2" 0 PLEXIGLASS
COLUMN 7' HIGH
LIQUID
SAMPLING
PORTS
(1/4" TUBING)
2'
1'
1'
1'
1'
1'
1'
2'
1'
SUBSTRATE
RESERVOIR
MEDIA
SAMPLING
PORTS
2 1/2" 0
SLUDGE RECIRCULATION
LINE
MEDIA
SCREEN (1" x 1" MESH)
EFFLUENT
SETTLING TANK
SLUDGE DRAIN

FIGURE 26

BENCH SCALE TRICKLING FILTER

## Aerated Lagoons

### Description of Process

Aerated lagoons are biological flow-through basins generally applicable when a high quality effluent in terms of suspended solids or organic concentration is not required. Aerated lagoons are more sensitive to temperature changes and biological upsets than activated sludge systems, but serve as good intermediate treatment processes.

Oxygen in aerated lagoons is supplied by diffused air systems or mechanical aeration devices, but the power level of the system is normally insufficient to keep all the biological solids in suspension. Solids deposition with subsequent anaerobic digestion is therefore common in aerated lagoon systems.

These systems may be considered as an interim treatment step in some cases because their organic removal capacity can be enhanced by converting to an activated sludge or extended aeration system by adding clarifiers, sludge return pumps, and additional aeration equipment.

### Design Considerations and Process Variables

1. organic loading
2. environmental factors (pH, temperature, *etc*.)
3. nature of wastewater and fluctuations in characteristics
4. level of mixing in aeration basin
5. nutritional requirements
6. basin depth and geometry
7. wind, heat transfer coefficient, humidity effects

### Preliminary Investigation Requirements

Aerated lagoons can be evaluated in the laboratory using a continuous reactor similar to that for activated sludge, but providing a strict flow-through system with no facilities for quiescent sludge settling. Aerated lagoons can be simulated on a pilot plant scale by using lined earthen tanks with small mechanical aeration equipment to supply oxygen and partial mixing.

## Waste Stabilization Ponds

### Description of Process

Waste stabilization ponds are biological processes which utilize bacteria and algae to fulfill the process treatment requirements. The available organic materials in the incoming waste are oxidized biochemically while algae, utilizing the simpler bacterial degradation products and sunlight, produce oxygen which is subsequently used by facultative and aerobic microorganisms.

If a high organic loading to a pond exerts an oxygen demand above that provided by photosynthesis and surface reaeration, anaerobic or facultative bacteria will predominate. When this occurs, alcohols, various forms of organic acids, and other miscellaneous degradation products of anaerobic degradation will be produced.

Many complex organic compounds not degraded in the conventional activated sludge process or aerated lagoons can be degraded in a waste stabilization pond because of the prolonged detention times. Therefore, it is feasible in many cases to use an aerated lagoon or activated sludge-waste stabilization pond system, especially where complex petrochemical or petroleum wastewaters are involved.

### Design Considerations and Process Variables

1. nature of wastewater organic & inorganic constituents
2. flow, detention time
3. surface loading
4. geometry and depth of pond
5. environmental conditions (pH, temperature, *etc.*)
6. geographical location
7. color, toxic materials, solids, *etc.*, of wastewater

### Preliminary Investigation Requirements

Waste stabilization ponds can be simulated in the laboratory using models and an artificial lighting system as shown in Figure 27. Both flourescent and incandescent lighting should be provided with an intensity of approximately 600-800 foot candles. A compressed air source should be affixed close to the liquid surface to simulate wind action. The organic removal efficiency at defined surface loadings and detention times can be estimated

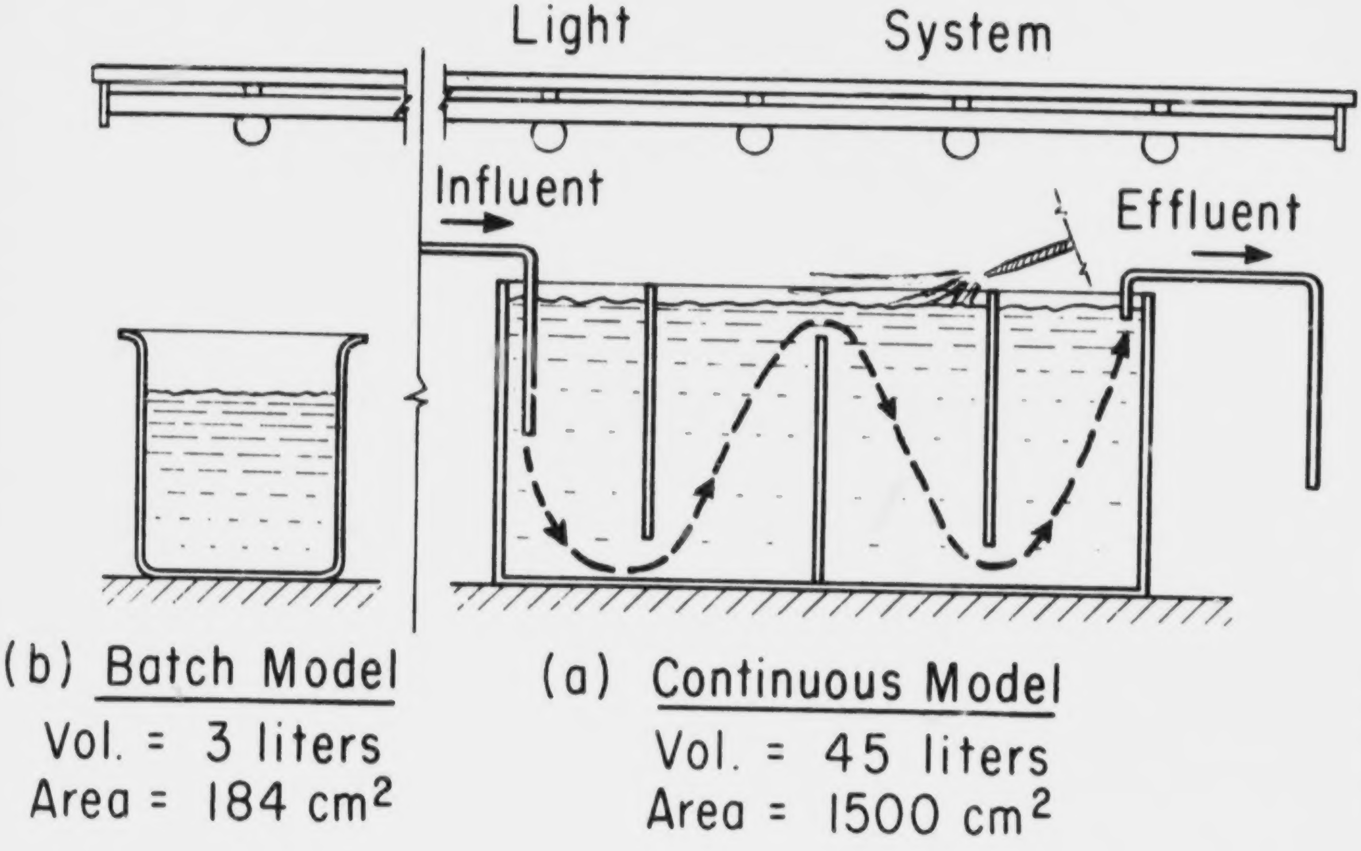
Light System
Influent
Effluent
(b) Batch Model
Vol. = 3 liters
Area = 184 cm²
(a) Continuous Model
Vol. = 45 liters
Area = 1500 cm²

FIGURE 27
WASTE STABILIZATION POND MODELS

using such a model as well as algal toxicity factors, environmental effects, etc. Larger scale test ponds can be constructed outside for conducting pilot studies if required.

## Chemical Oxidation (Ozone Treatment)

### Description of Process

Wastewaters discharged from many petrochemical or refinery processes are complex and highly resistant to biological degradation. This necessitates some alternate form of secondary treatment. Chemical oxidation using ozone has proved effective for specific wastewaters.

The chemical oxygen demand (COD) of a wastewater containing unsaturated organic compounds can be reduced by ozone oxidation, and the effectiveness of this reduction in terms of ozone utilization can be defined as the number of oxygen atoms reacting with the waste constituents with the consequent reduction in COD per ozone molecule adsorbed (Kwie, 1969). Depending on the extent of oxidizable or unsaturated compounds in the waste, one or all three of the oxygen atoms per ozone molecule can remain chemically attached to the waste constituent during ozonation.

### Design Considerations and Process Variables

1. nature of the organic materials (amount of unsaturates)
2. the pH of the wastewater
3. voltage and rate of oxygen flow-through
4. the ozone generator
5. type of ozone distribution system

### Preliminary Investigation Requirements

The amenability of wastewater to ozone oxidation can be evaluated using bench scale apparatus shown in Figure 28 (Eckenfelder and Ford 1970). The ozone-oxygen gas is bubbled through the wastewater sample contained in the reaction flask. The ozone utilization and the corresponding COD reduction then can be evaluated in terms of an oxygenation factor: $\left[\frac{\text{lbs COD removed}}{\text{lbs ozone used}}\right]$.

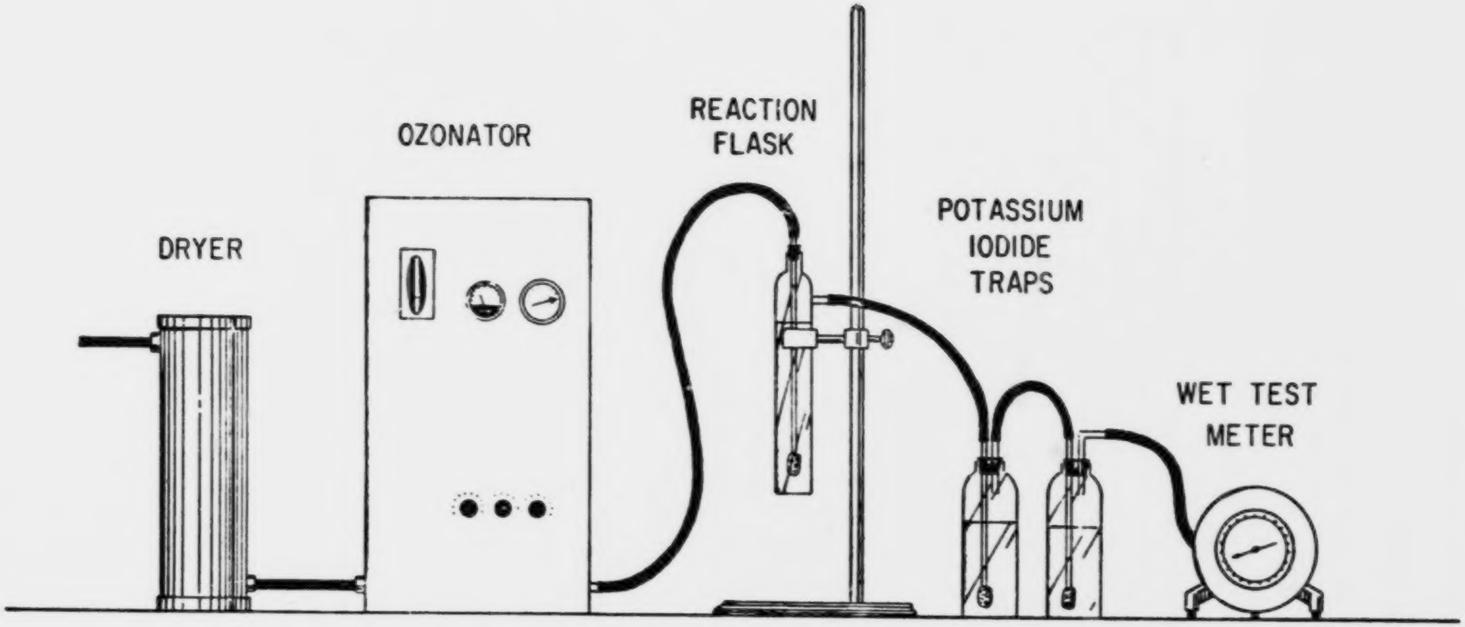
DRYER
OZONATOR
REACTION FLASK
POTASSIUM IODIDE TRAPS
WET TEST METER

FIGURE 28

LABORATORY SCALE OZONE TREATMENT

## Nitrification - Denitrification

### Description of Process

The 2-stage conversion of ammonia to nitrate by microorganisms is well documented (Delwiche, 1956; Henrici and Ordal). This nitrification process is influenced by the substrate or carbon loading, the temperature, and the pH. As these and other variables are critical with respect to the oxidation reactions, the design of nitrification tanks must incorporate these factors.

The removal of nitrogen from nitrified effluents can be effected using biological denitrification methods (Sawyer and Bradney, 1945; McKinney and Conway, 1957; Symons and McKinney, 1958). This is an anaerobic process and is likewise sensitive to many environmental stresses. It is the opinion of many investigators that a series nitrification-denitrification system is a practical method for nitrogen removal (Wuhrmann, 1962; Oechsner). However, when comparing this method of nitrogen removal to alternate systems such as ammonia stripping or ion exchange, it is necessary to consider all the variables which affect the efficiency of the process, the operational problems involved, the quality of the effluent required with respect to total nitrogen, and the process economics.

### Design Considerations and Process Variables

1. organic loading
2. environmental factors (pH, temperature, etc.)
3. mixed liquor dissolved oxygen
4. concentration and form of influent nitrogen
5. sludge age
6. aerobic detention time (nitrification) and anaerobic detention time (denitrification)

### Preliminary Investigation Requirements

Nitrification and denitrification have been evaluated using both bench scale and pilot scale studies (Balakrishnan and Eckenfelder, 1968; Oechsner; Barth, et al, 1968).

Bench scale studies involve the use of continuous reactors and trickling filters to obtain nitrification, varying influent carbon, nitrogen, and altering environmental conditions in order to determine the effect of process variables on nitrification rates and capacities. Pilot scale use of filters and aeration tanks have been similarly applied.

The aspects of biological denitrification can be assayed using continuous bench or pilot scale reactors with mechanical mixing devices. The mixing levels should be sufficient to maintain a relatively homogeneous mixture of biological solids and substrate but not capable of introducing oxygen to the liquid. Again, process variables such as influent nitrate and carbon concentration, mixed liquor solids, etc., are controlled in order to evaluate their effects.

## TERTIARY TREATMENT

The treatment of wastewaters by conventional primary and secondary processes does not yield an effluent of sufficient quality to meet the necessary criteria in many instances. Tertiary or advanced wastewater treatment processes consequently are required to remove these residual or refractory contaminants.

Tertiary treatment processes are utilized to remove residual suspended solids, including microorganisms, dissolved solids, complex organics, and other pollutants such as nitrogen and phosphorus compounds, and ABS. The tertiary treatment processes as categorized in Table 17 are listed herein and are described in terms of their treatability or preliminary investigation requirements.

### Chemical Coagulation - Precipitation*

#### Description of Process

Chemical coagulation-precipitation can be employed either as a primary treatment or tertiary treatment step, depending on the contaminants present and the desired level of removal. Lime precipitation as a tertiary process for the removal of phosphorus and organic carbon is considered in this section.

The lime precipitation system may be designed either as a 2-stage lime process with lime addition to pH 11.5 in the first stage followed by recarbonation to pH 9.5 to 10 with flocculent additives in the second stage, or as a single-stage lime process at pH 11.5 with sodium carbonate added to reduce excess calcium ions (O'Farrell, Bishop, and Bennett, 1968). The application of this system in polishing effluents from a secondary plant treating petrochemical or refinery wastewaters would have to be verified either by bench scale or pilot scale studies as the multiplicity of contaminants present in such wastewaters could interfere with the coagulation-precipitation reactions.

---

* This process is interchangeable with Pre or Primary Treatment by Coagulation-Precipitation.

### Design Considerations and Process Variables

1. flow
2. concentration and nature of the contaminants
3. concentration of coagulant
4. detention time of mixing and clarification zones
5. dissolved oxygen and carbon dioxide concentrations
6. chemical purity of coagulant
7. temperature and pH of the liquid mixture

### Preliminary Investigation Requirements

Bench scale tests using a batch "jar test" procedure can be used, determining the optimum dosage and pH by varying parameters and monitoring the contaminant removal for each condition (Eckenfelder and Ford,1970). A continuous pilot plant simulation, although more costly, would yield more dependable data. The range of operating temperatures, coagulant dosages, and pH values, with respect to contaminant removal, however, can be determined in bench scale jar tests, using this information to establish pilot plant operating conditions.

## Gas Stripping

### Description of Process

Stripping essentially is a form of distillation wherein a small amount of a relatively volatile material is removed from a large volume of less volatile material (Manual on Disposal of Refinery Waste, Vol on Liquid Waste, 1969). In refinery waste disposal, the process is generally used for removing small amounts of volatile impurities, *e.g.*, hydrogen sulfide, ammonia and cyanide from large volumes of wastewaters. The method is not suitable for removing materials of low volatility, such as phenolics, because heating and equipment requirements make it uneconomical. The most frequent use of stripping in refinery waste disposal is for removal of hydrogan sulfide and ammonia from foul waters.

Gas stripping may be considered tertiary treatment or pretreatment. For example, in the refinery industry, it is considered part of pretreatment whereas in domestic wastewater treatment it may be considered tertiary treatment. Stripping is a modification of the aeration process. The process may be utilized to remove both ammonia and hydrogen sulfide under proper conditions of temperature and pH. Air requirements for ammonia removal may be decreased by the inclusion of a pre-concentration step utilizing zeolyte absorbents. Lime is normally used as a hydroxide source in the ammonia removal process.

When the removal of hydrogen sulfide is desirable, a stripper can be applied. An acidic condition is necessary for the efficient stripping of sulfides. Ammonia stripping necessitates alkaline conditions as none of the ammonia is in the gaseous state below pH seven.

Gas stripping is generally conducted in a packed tray tower equipped with air blower. The towers usually are designed so that the gas and liquid leaving a desorption plant are in contact with gas containing little or no vapor absorbed from the liquid (Bayley, 1967). The wastewater is pumped to the top of the packed tower where it is distributed uniformly over the packing through which a steady stream of air or gas is drawn.

### Design Considerations and Process Variables

1. waste flow
2. contaminant concentration
3. hydrogen ion concentration of wastewater
4. wastewater temperature
5. aeration transfer equipment
6. contact time
7. waste loading
8. air flow rate
9. nature and size of packing material
10. diameter of column
11. height of column
12. operating pressure and temperature in column

### Preliminary Investigation Requirements

The first step in the design of a stripping column is to fix its internal diameter. A permissible average gas rate of

400 cubic feet per gallon may be assumed. For packed columns this permissible rate is determined by flooding conditions for a given plate efficiency. The internal diameter of the column can be calculated directly from the permissible gas rate and the volume of waste liquid to be passed through the column. Diameters usually vary between three to six feet with the height being determined by the equilibrium conditions in the column and by the number of contacts necessary for the amount of stripping desired. The realtionship between mass transfer coefficients determined in the laboratory or from pilot plant data and corresponding coefficients for full-sized towers have been studied exhaustively (Bayley,1967). Provided conditions of flow in both systems are turbulent, the performance of the full-scale unit may be estimated quite rapidly from pilot plant information. A bench scale stripping tower is shown in Figure 29.

## Microscreening

### Description of Process

Microscreening, or microstraining, is a form of simple filtration. The objective is the clarification of liquids by the removal of suspended solids, especially those of microscopic size. The process involves the use of a horizontal, rotating drum-type straining element whose periphery is enveloped with perforated or mesh-type screening material. In use, a thin mat forms over the fabric screen and as the wastewater enters the drum and passes through the mesh fabric in radial directions, solids are strained from the wastewater. The solids are retained on the inside surface of the fabric and continually backwashed to waste. The drum may be installed in a concrete or steel box. The weight or volume of particles intercepted varies with the cube of the screen apertures and therefore significant differences in efficiency are obtained by using varying mesh sizes. This process has been investigated as a potential pretreatment method preceding carbon adsorption, distillation, solvent extraction, reverse osmosis, freezing, and electrodialysis.

### Design Considerations and Process Variables

1. flow
2. suspended solids
3. nature and sizes of suspended solids
4. variation of suspended solid concentrations

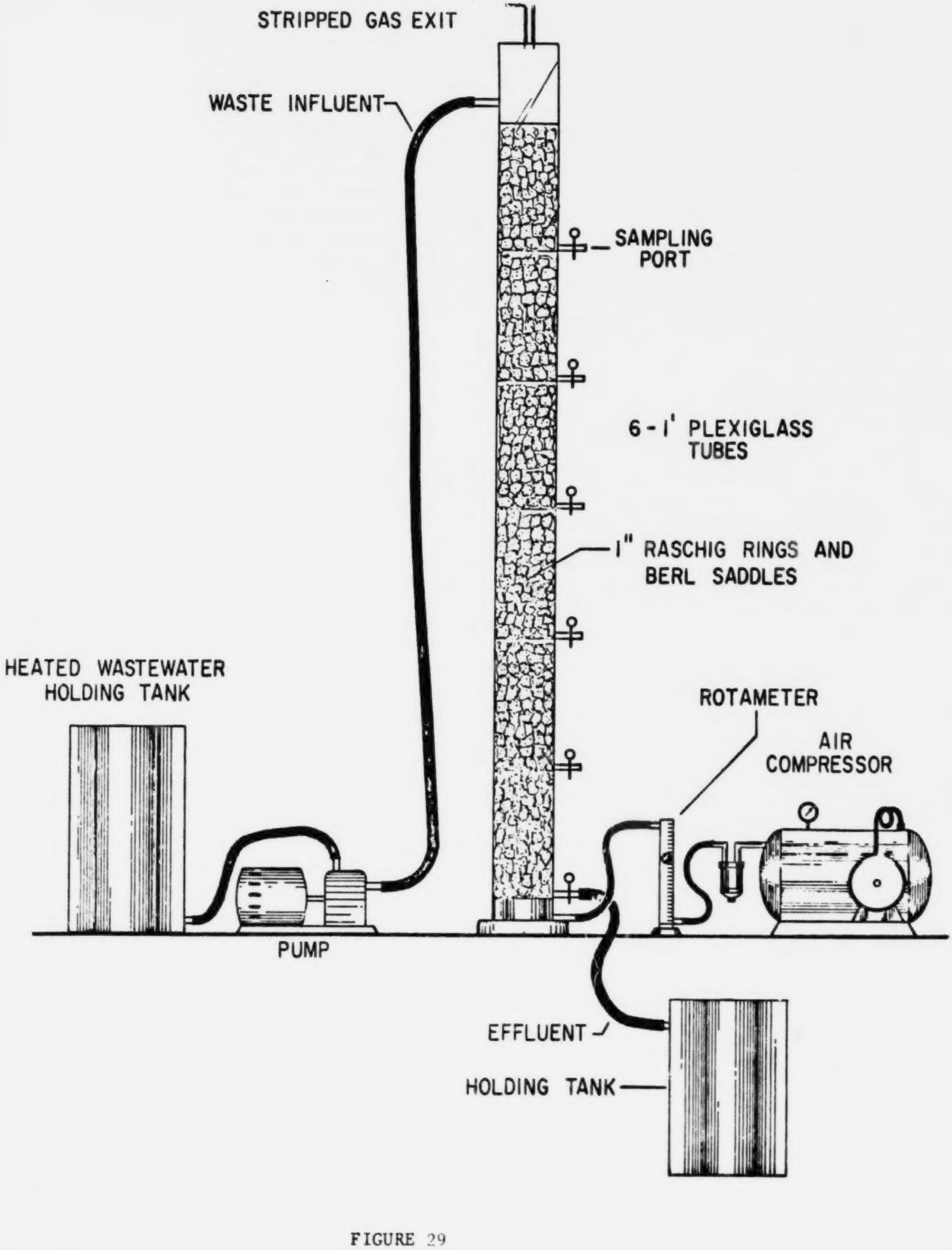
STRIPPED GAS EXIT
WASTE INFLUENT
SAMPLING PORT
6 - 1' PLEXIGLASS TUBES
1" RASCHIG RINGS AND BERL SADDLES
HEATED WASTEWATER HOLDING TANK
ROTAMETER
AIR COMPRESSOR
PUMP
EFFLUENT
HOLDING TANK

FIGURE 29

BENCH SCALE GAS STRIPPING TOWER

5. filtration area and rotation speed

6. presence of oil, grease, or other floatables

7. filter fabric mesh size

### Preliminary Investigation Requirements

A microstraining plant cannot be designed in the same manner as a rapid sand filtration plant (Boucher and Evans). Rates of flow through the filtering media are much higher than through sand beds; frictional resistance allowable is much less; and the fabric is matted very rapidly by the solids intercepted. The rate of filter blockage is measured in terms of filterability, and this is designated as the filterability index (I). Given this index from samples of the water in its poorest condition of suspended solids applied and the grade of fabric employed, the general problem of design is to determine the dimensions of the strainers and rotation speeds required to pass the required rate of flow.

The calculation of the filterability index may be performed in many ways. The most accurate method is with the apparatus devised by Boucher (1947), a laboratory set-up that measures the head loss across a section of the filter being tested using the waste in question. Another device has been developed for field use but has been found to be less reliable (Bodien and Stenburg, 1966).

Suspended solids removals appear to be relatively unaffected by feed concentration and removal efficiencies on the order of 85 to 90 percent may be expected. The microscreening process may best be evaluated on a pilot scale.

## Carbon Adsorption

### Description of Process

Adsorption of molecules from the liquid phase to the solid phase occurs as the result of either electrical attraction of the solute to the adsorption surface, Van der Waals forces, chemical reactions, or possibly a combination of these phenomena. The type of adsorption associated with the removal of organics is generally caused by Van der Waals forces or "physical" adsorption and usually occurs in three phases: the transport of the contaminant (adsorbate) to the exterior surface of the adsorbing media (adsorbent); the diffusion of the adsorbate into the pores of the adsorbent; and the adsorption of the adsorbate on the surface of the adsorbent. Activated carbon, carbonaceous material with certain adsorptive and catalytic properties, has an affinity for many contaminants present in petrochemical or refinery wastewaters, and contact between the carbon surfaces and the waste is achieved through fixed-bed or expanded-bed carbon columns. Once breakthrough in the volumn occurs (the column is in equilibrium with the wastewater), the spent carbon is either wasted or regenerated for subsequent use.

### Design Considerations and Process Variables

1. flow rate
2. contact time
3. depth of carbon bed
4. adsorptive capacity of adsorbent
5. influent solute concentration
6. allowable effluent solute concentration
7. particle size
8. environmental factors (temperature, pH, *etc.*)

### Preliminary Investigation Requirements

Adsorption rates and general relationships can be formulated using batch contact reactors or continuous columns. Carbon is usually added to batch systems in powdered form and removed by flocculation and sedimentation. This can be simulated in the laboratory using test flasks and a shake assembly. The weight of carbon added and the corresponding removal of organic material for varying conditions is then translated into one of the isotherm equations.

Serial continuous carbon columns usually offer the most practical system for the polishing of effluents as the separation of carbon from the wastewater after contact is not required. The concentration of the adsorbed solute is in equilibrium with the influent concentration rather than the effluent solute concentration enhancing removal, and greater flexibility of operation is possible.

## Electrodialysis

### Description of Process

This process is based on the migration of positively charged ions and negatively charged ions to respective oppositely charged electrodes and on the ability of semi-permeable membranes to selectively permit the passing of ions of one type of charge while repelling ions of the opposite charge. Electrodialysis is specifically for ions and the membranes are essentially impermeable to water.

The electrodialysis process is a form of tertiary treatment and must be preceded by additional tertiary treatment including filtration. Non-ionized molecules and suspended solids are not removed during the process, and, if present, will cause membrane fouling (Brunner, 1967). Sulfuric acid is used in the process to abate membrane fouling, and the apparatus is arranged so that concentrated and diluted streams flow continuously. Only partial demineralization by this method is practical, however, because electrical power requirements become excessive if the ion concentration is reduced too far ("Summary Report - Advanced Waste Treatment Research" 1962 to 1964). The power consumption is also a function of the amount of ions that must be removed. Single-pass electrodialysis will reduce the total dissolved solids concentration in water by about 40 to 50 percent.

## Design Considerations and Process Variables

1. membrane
    a. size
    b. area utilization
    c. current density
    d. thickness
    e. resistance
    f. bursting strength
    g. liquid velocity
    h. space between membranes
    i. headloss through stack
2. stack design
    a. flow
    b. ionic characteristics of wastewater
    c. influent and effluent ionic concentration
    d. pH and stability of feed water

### Preliminary Investigation Requirements

The removal of inorganics may be defined by Farraday's Law. The determination of electrical resistance and energy consumption requires the knowledge of certain constants related to the particular equipment used, the water, and temperature. These design parameters may be determined through use of pilot plant studies ("Electrodialysis in Advanced Waste Treatment", 1967). Such an electrodialysis pilot unit is shown in Figure 30.

## Ion Exchange

### Description of Process

Ion exchange is an exchange adsorption process in which ions associated with the solid adsorbent are exchanged for ions in solution and is used to remove undesirable anions and cations from wastewater. Most ion exchange resins presently used are synthetic resin materials consisting of a network of hydrocarbon radicals to which are attached soluble ionic functional groups. The total number of functional groups per unit weight of resin determines the exchange capacity and the group type determines the exchange equilibrium and the ion selectivity. Ion exchange resins may be strong or weak acidic cation exchangers or strong or weak basic anion exchangers. Generally, hydroxyl ions are exchanged for the anions removed from solution while hydrogen or sodium ions are replaced by the cations which are taken up by the exchange media.

### Design Considerations and Process Variables

1. applied feed rate per unit volume of resin
2. exchanger depth
3. backwash expansion
4. flow rate per unit area of resin
5. regenerate flow rate
6. rinse water flow rate
7. regenerate concentration
8. nature of resin

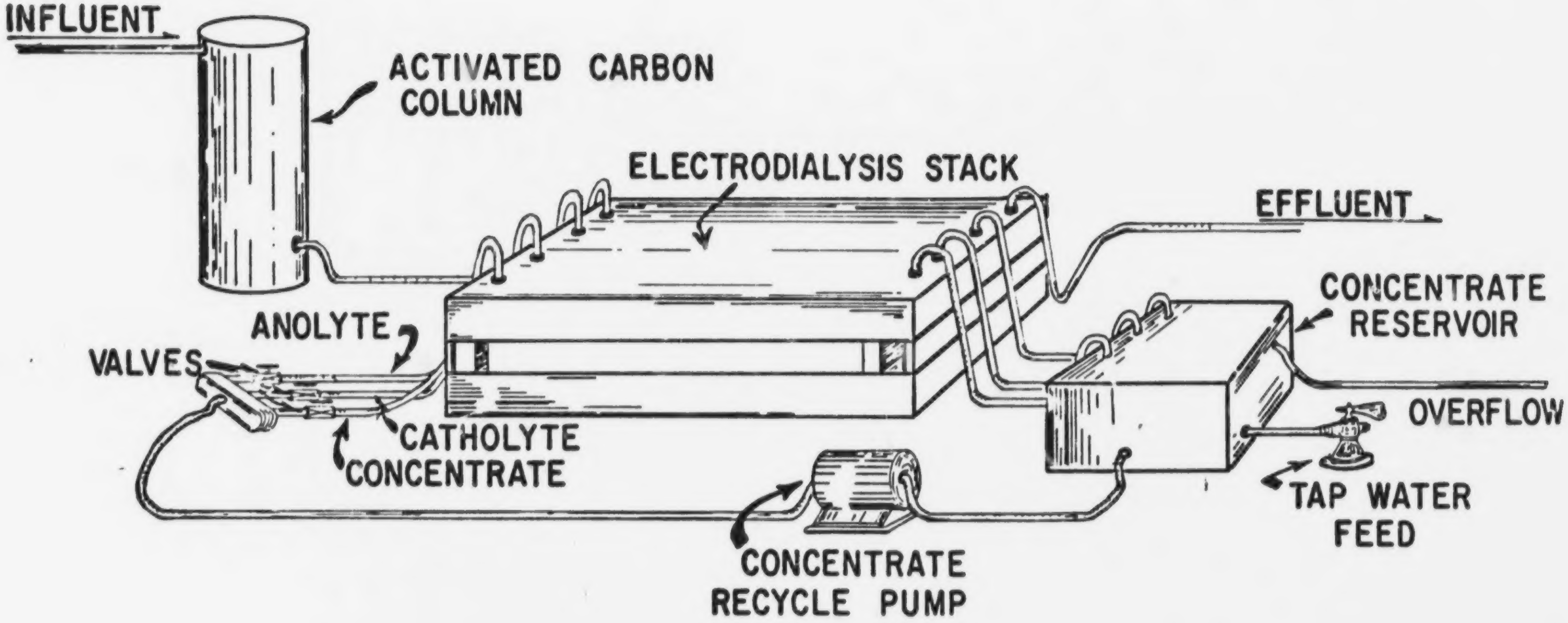
INFLUENT
ACTIVATED CARBON COLUMN
ELECTRODIALYSIS STACK
EFFLUENT
ANOLYTE
VALVES
CATHOLYTE
CONCENTRATE
CONCENTRATE RESERVOIR
OVERFLOW
TAP WATER FEED
CONCENTRATE RECYCLE PUMP

FIGURE 30

LABORATORY ELECTRODIALYSIS UNIT

### Preliminary Investigation Requirements

An ion exchange column as shown in Figure 31 can be used to develop data necessary for design of prototype ion exchange units. Based on the observed number of ion equivalents removed per unit time, the resin volume requirement can be estimated. Additionally, the rinse water and regenerate requirements can be predicted (Eckenfelder and Ford, 1970).

## Evaporation

### Description of Process

Evaporation is a process by which liquid is changed to vapor. Although molecules of water are continuously leaving the water surface, others are returning, and the rate of evaporation is determined by the net accumulation of those leaving the water surface. If the temperature of the surface is to be maintained, large quantities of heat must be supplied by radiation and conduction from the overlying air or at the expense of any heat stored below the surface.

Evaporation may be accomplished in special equipment designed for this specific purpose. However, the process is relatively expensive and is limited primarily to the recovery of colatile by-products from waste liquids and to the treatment of wastewaters where no alternate methods are available. This discussion will be concerned with evaporation by natural environmental effects.

The evaporation process in its simplest form consists of providing shallow reservoirs and allowing the wastewater to be detained until the transformation of the liquid to vapor has been completed.

### Design Considerations and Process Variables

1. effective surface area
2. temperature of the water and of the air
3. the movement of air above the water surface
4. the relative humidity
5. nature of the wastewater
6. depth of the reservoir

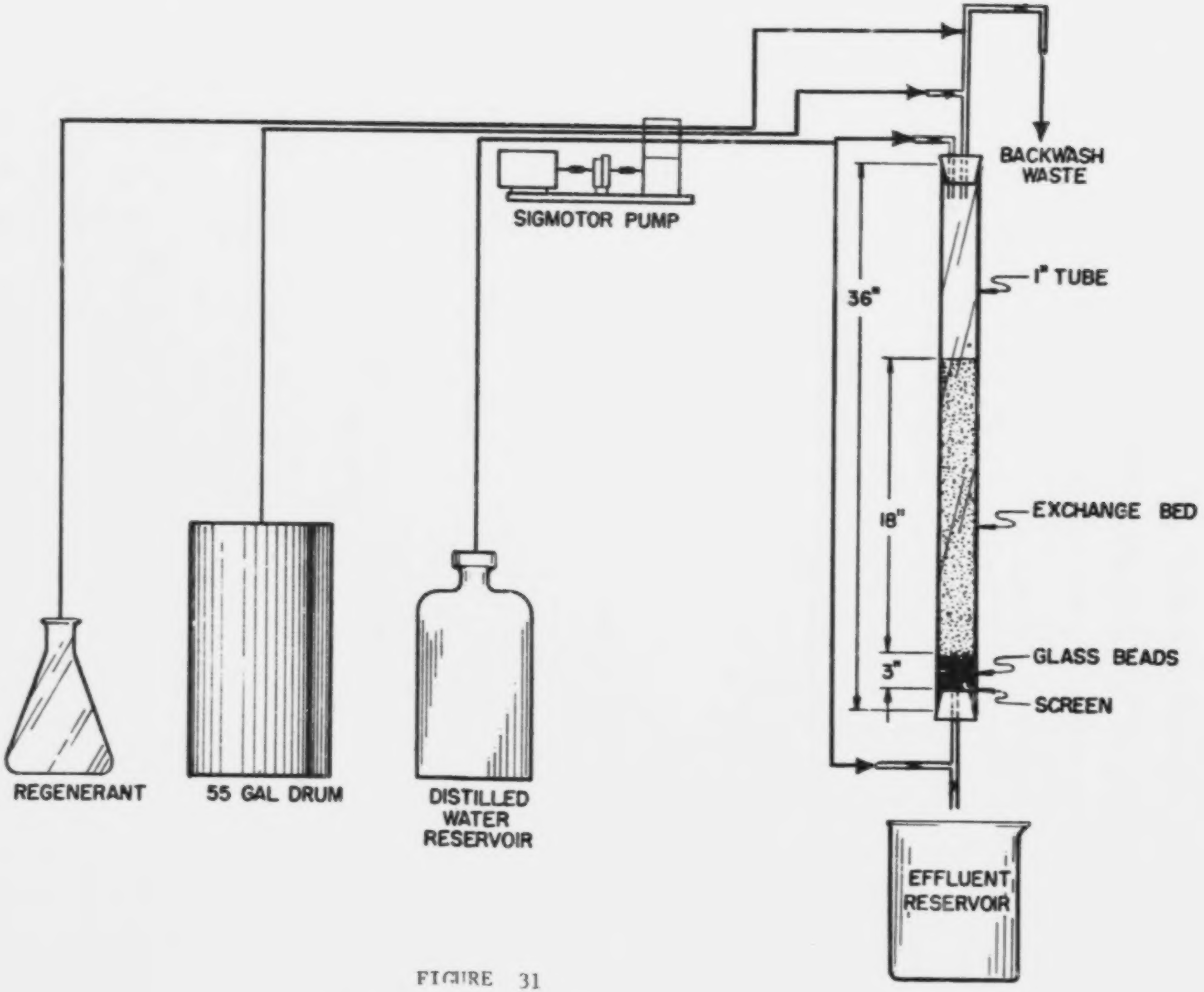
BACKWASH WASTE
1" TUBE
36"
18"
3"
EXCHANGE BED
GLASS BEADS
SCREEN
SIGMOTOR PUMP
REGENERANT
55 GAL DRUM
DISTILLED WATER RESERVOIR
EFFLUENT RESERVOIR

FIGURE 31

LABORATORY ION EXCHANGE COLUMNS

7. salinity of the wastewater

8. concentration of surfactants or other evaporation suppressents in the wastewater

9. precipitation

10. geographic location

### Preliminary Investigation Requirements

The predictor equation mentioned herein was derived from work conducted by the Bureau of Agricultural Engineering of the United States Department of Agriculture (Rohwor, 1931). Many other formulas have been proposed by different experimenters for the determination of the rate of evaporation from free water surfaces, but little information concerning evaporation of wastewaters is available. However, basic design criteria can be established by use of evaporation pans. The standard Weather Bureau Class A Pan is the most widely used in the United States. The Pan is filled to a depth of 8 inches and the water surface level is measured daily for evaporation determinations. Other measuring equipment should be available at the Pan site for meteorological determinations and evaluation of other factors contributing to evaporation.

## Reverse Osmosis

### Description of Process

A natural phenomenon known as osmosis occurs when solutions of two different concentrations are separated by a semi-permeable membrane ("Summary Report - Advanced Waste Treatment Research", 1962 to 1964). With such an arrangement water tends to pass through the membrane from the more dilute side to the more concentrated side. The driving force that imparts this flow through the membrane is related to the osmotic pressure of the system, and this pressure is proportional to the difference in concentration between the two solutions. When pressure is applied to the more concentrated solution, the flow of water can be retarded or even reversed, i.e., water moves from the more concentrated compartment to the less concentrated compartment. The properties of a membrane that permit water molecules to pass through but impede the flow of contaminant molecules are not clearly understood, but membranes composed of modified cellulose acetate prepared with various inorganic additives exhibit this separability. The reverse osmosis process provides an affirmative barrier to viruses, inorganics and refractory organics, and removes unionized as well as ionized materials.

Reverse osmosis, which is a form of tertiary treatment, should be preceded by additional treatment including filtration. Secondary effluent is pumped under a pressure exceeding the osmotic pressure into a high pressure vessel separated from a collection vessel by a semi-permeable membrane. The product water is collected on the low pressure side of the membrane, usually at atmospheric pressure, and the concentrated brine from the high pressure vessel is discharged to waste. Synthetic osmotic membranes are available which can reduce the total dissolved solids concentrations of saline feed waters from 50,000 mg/l to 500 mg/l.

## Design Considerations and Process Variables

1. water flux (gallons/square feet/day through the membrane)
2. membrane area, square feet/cubic feet
3. salt rejection, percent
4. operating pressure, psi
5. flow
6. total dissolved solids concentration of feed
7. acidity and fouling characteristics of waste
8. salt removal efficiency

## Preliminary Investigation Requirements

Laboratory systems data are only partially representative of the performance of larger reverse osmotic systems. Membrane surface area is smaller in laboratory systems and less likely to contain imperfections. Flow regimes and patterns in the laboratory desalination cell may differ from those present in larger systems. Rejection increases with pressure and therefore comparisons between laboratory and pilot plant performance may be misleading if the operating pressures are not considered (Golf and Gloyna, 1969). Process requirements may readily be determined from pilot plant operation and with care, laboratory studies may be used to evaluate the feasibility for such operations. Four types of reverse osmotic units have been tested: plate and frame, spiral, tubular, and hollow fine fiber. A tubular laboratory unit is shown in Figure 32 .

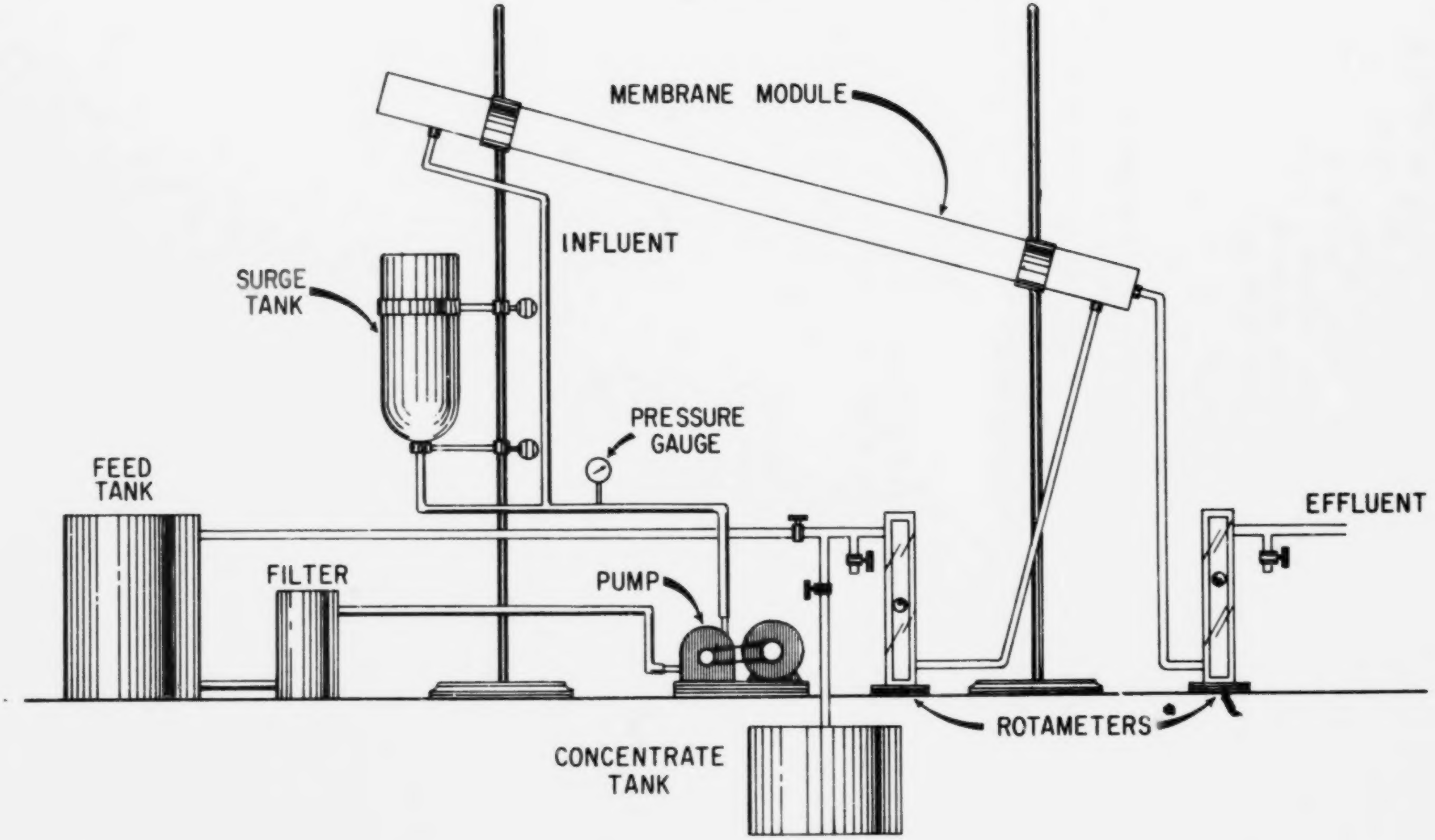
MEMBRANE MODULE
INFLUENT
SURGE TANK
PRESSURE GAUGE
FEED TANK
EFFLUENT
FILTER
PUMP
ROTAMETERS
CONCENTRATE TANK

FIGURE 32

LABORATORY TUBULAR REVERSE OSMOSIS UNIT

## Disinfection by Chlorination

### Description of Process

Chlorination has long been considered to have the greatest practical potential of all disinfection systems for freeing wastewaters of pathogens (Rhines. 1968). Other agents have been proposed for disinfection such as bromine and iodine. Ozone has been effective for disinfection of water supplies and disinfection may also be accomplished by the use of electromagnetic radiation.

Although chlorine is primarily used as a disinfectant, its use may also be considered a form of tertiary treatment in that residual organics are oxidized by free chlorine. As a result of the strong oxidizing power of chlorine, this element will destroy or inhibit the growth of bacteria and algae. Metal ions which are in their reduced state react with chlorine and are also oxidized.

The type and amount of chlorine compound in solution is pH and temperature dependent. Initially, chlorine added to wastewater is reduced by compounds which react rapidly with the chlorine. Finally, when all chlorine-reducing substances are oxidized in the wastewater, the additional quantity of chlorine added to the water results in an equivalent residual chlorine. The residual chlorine is the form which is necessary for effective disinfection.

Chlorination may be accomplished by the addition of gaseous chlorine or by the addition of calcium or sodium hypochloride. Disinfection is time dependent and it is normally necessary to provide a detention period of 20 to 30 minutes to provide effective disinfection and also to account for short-circuiting in the detention basin. Disinfection of a wastewater effluent is indicated by a chlorine residual which may be detected in the effluent after sufficient contact time.

### Design Considerations and Process Variables

1. flow
2. hydrogen-ion concentration of the wastewater (pH).
3. extent of chlorine reducing compounds in the wastewater
4. form and concentrations of nitrogen compounds in the wastewater
5. chlorine demand
6. chlorine feed concentrations

7. contact time

8. temperature

9. nature and number of organisms in the water

### Preliminary Investigation Requirements

Basic design criteria for disinfection by chlorination can be established through laboratory techniques. The objective of the laboratory procedure is to relate contact time, chlorine dosage, and chlorine residual to effective disinfection. The Coliform family of bacteria is normally used as an indicator of contamination and their degree of removal may be related to disinfection efficiency. The contact time determined from the laboratory procedure is normally increased to account for short-circuiting and other difficulties encountered in actual plant operation. Wastewater treatment facilities normally require between 3 and 15 mg/l of chlorine for disinfection, and it is customary to carry a 1 mg/l residual measure in the effluent after a 20-minute chlorine contact period.

## Rapid Sand Filtration

### Description of Process

Rapid sand filtration can be used effectively to polish secondary wastewater effluents. Rapid sand filtration may be accomplished by gravity and under pressure, but gravity sand filters handle large flows more economically.

The conventional rapid sand filter consists of 18 inches of gravel overlain by 30 inches or less of sand. Natural silica sand is a common filtering medium, but other fine grained filter materials such as crushed anthracite have been used. The rapid sand filter is normally rectangular in shape and reinforced concrete construction is commonly used for housing the filter beds. The filter beds are underlain with a piped lateral collection system and the installation is valved to permit backwashing and to control the application of wastewater to the beds. Conventional filters are operated at hydraulic loadings in thr range of two to four gpm/ft$^2$. Rapid sand filtration has been enhanced by the use of multimedia filters incorporating, for example, sand-coal-garnet beds and hydraulic loadings of four to eight gpm/ft$^2$ are commonly used in these multimedia beds.

## Design Considerations and Process Variables

1. flow rate
2. media grain size
3. filter depth
4. properties of suspended solids
5. temperature
6. use of chemical treatment and filter aids
7. filter hydraulic loading, gpm/ft$^2$
8. allowable headloss to the bed

## Preliminary Investigation Requirements

Rapid sand filtration is affected by a large number of variables and at the present time, there is no accepted mathematical model that correlates all the variables affecting the filtration phenomenon.

In general, it seems that because so many variables affect the removal of solids and sand filters, all of them cannot be included in one filtration equation. Floc size, size distribution, shape, composition and concentration, together with sand size and shape, size distribution, rate of filtration, temperature, etc., all play a part in determining the manner and extent to which suspended solid removal is accomplished in a given filter layer. Therefore, filter design still remains the "art of relaying past experience to the prediction of filter performance" (Fox and Cleasby, 1966).

The rapid sand filtration process lends itself to pilot plant study and many of the variables can be evaluated in the laboratory. Figure 33 illustrates a laboratory-sized rapid sand filtration unit.

## SLUDGE HANDLING AND DISPOSAL

Sludge dewatering and disposal is one of the more important components of the total waste treatment system. Not only are large quantities of waste solids accumulated daily, but the day-to-day cost of sludge disposal frequently exceeds the cost of any other single process in a wastewater treatment plant. Primary sludges from refinery wastewaters are among the most difficult to handle due to the presence of oils and emulsions.

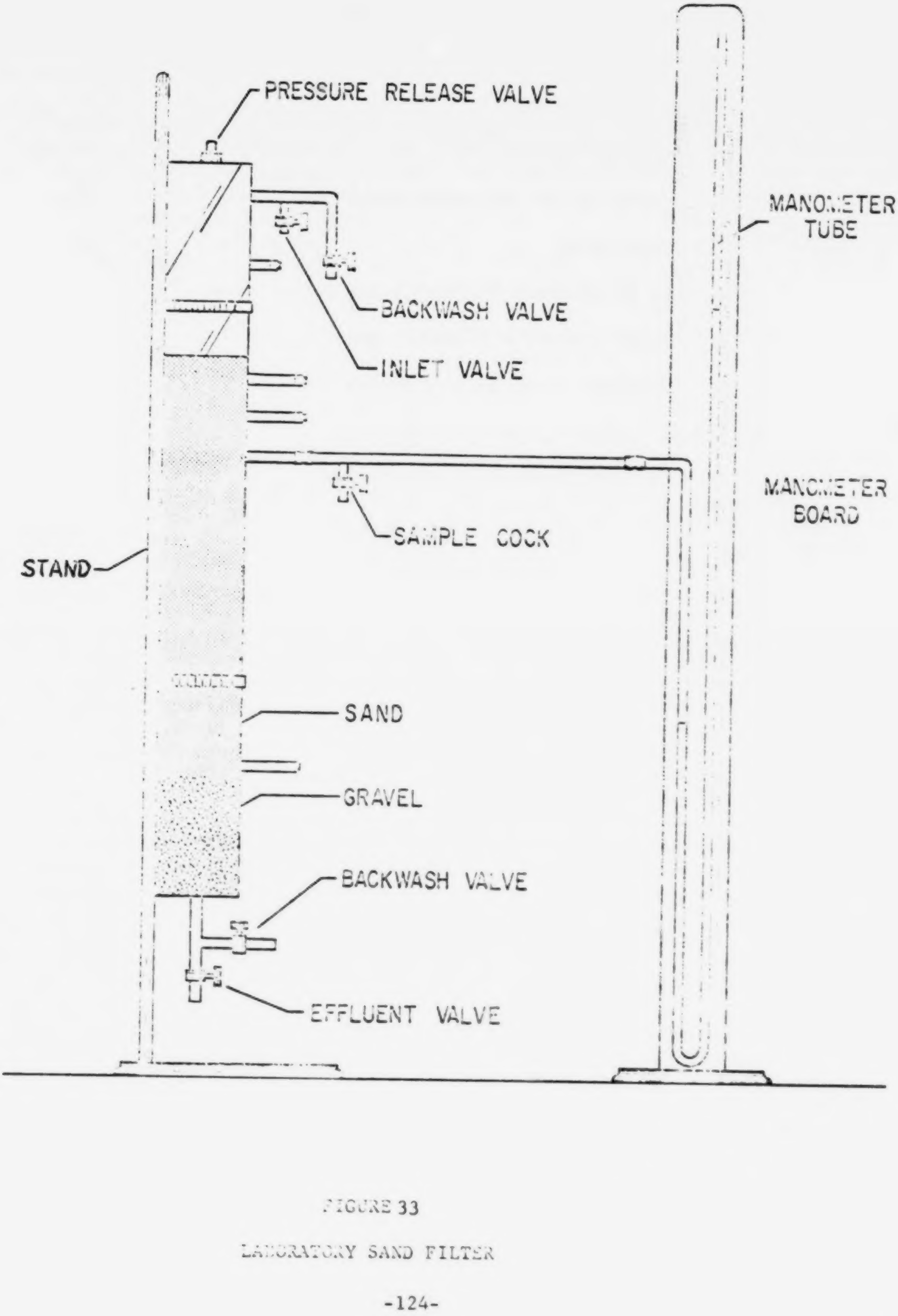
PRESSURE RELEASE VALVE
MANOMETER TUBE
BACKWASH VALVE
INLET VALVE
MANOMETER BOARD
SAMPLE COCK
STAND
SAND
GRAVEL
BACKWASH VALVE
EFFLUENT VALVE

FIGURE 33

LABORATORY SAND FILTER

Sludge handling and disposal includes concentrating the sludge for process use, dewatering and processing the sludge for conversion into a form suitable for disposal, transportation of the sludge, and final disposal.

Characterizing sludge handling methods is extremely difficult as two or more processes may be used conjunctively for one operation. In the past, anaerobic digestion was widely practiced in the treatment of primary sludges and thickened secondary sludges. However, few anaerobic digesters are presently used in refinery or petrochemical wastewater treatment facilities. Mechanical dewatering of sludges is being adopted by increasing numbers of cities and industries due to increasing land and labor costs. Barging of thickened sludge to the ocean is being practiced by municipalities and industries near coastal areas, but this method may be restricted in the future. Sludge incineration, therefore, is considered the process having the most potential ("A Study of Sludge Handling and Disposal", 1968).

Often sludge handling and disposal represents 25 to 50 percent of the total capital and operating cost of a wastewater treatment plant and the volume of waste sludge will continue to increase. Sludge handling and disposal is an integral part of the total waste treatment process and required the same degree of study given to other plant processes. Predictor equations may be more difficult to derive for sludge handling operations; however, through the use of laboratory and/or pilot plant equipment, basic design criteria can be established.

Analyses helpful in characterizing wastewater sludges with regard to handling and disposal are schematically presented in Figure 34 . The sludge fractions are categorized as inorganic and organic, with a suggested sub-categorization of the organic component into its biological and non-biological fractions. As the effects of benthic sludges, effluent suspended sludges, and excess sludge for disposal are environmentally significant, it becomes necessary to quantitatively and qualitatively evaluate its biological composition.

The sludge handling and disposal treatment processes as categorized in Table 17 are listed herein and are described in terms of their treatability of preliminary investigation requirements.

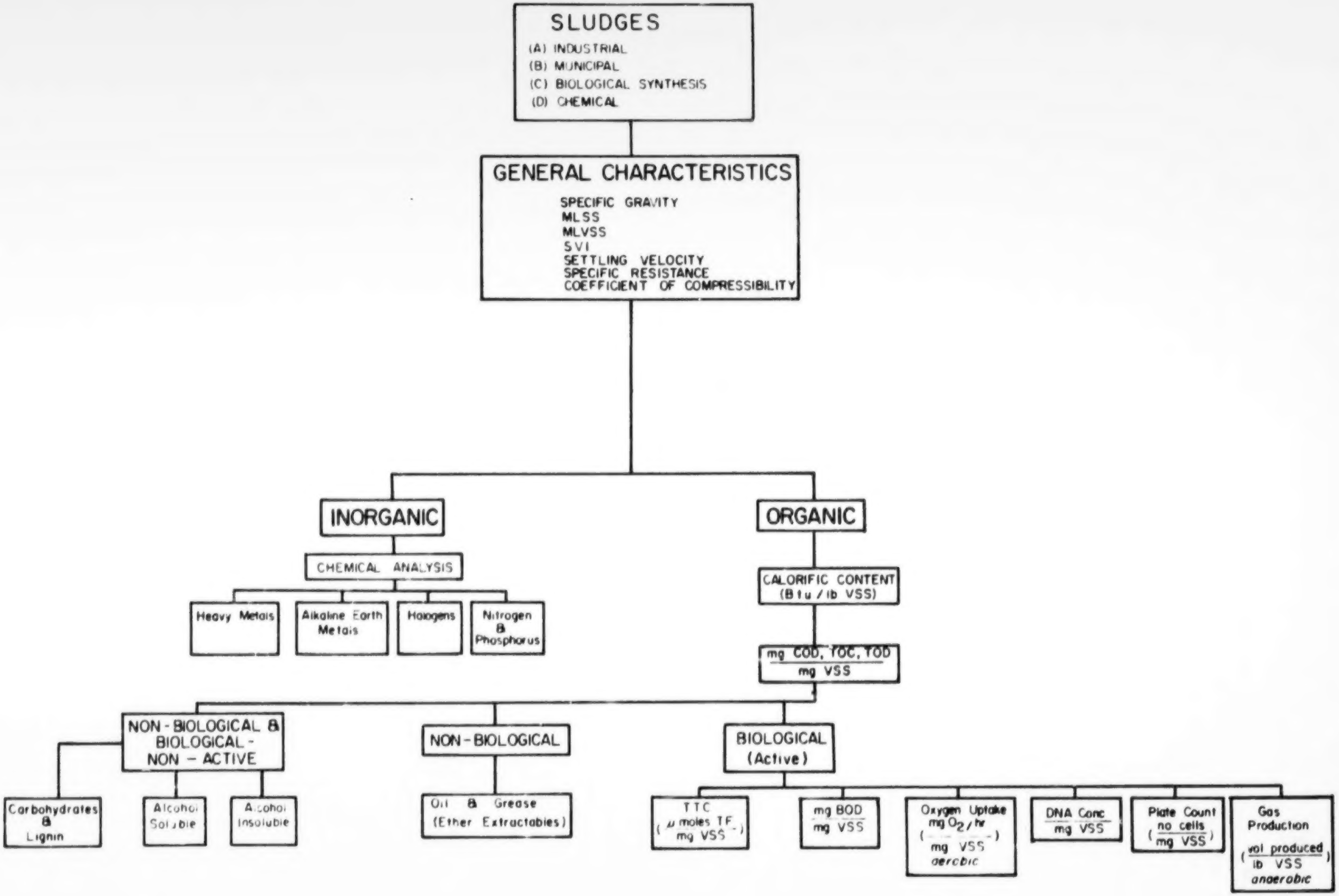
SLUDGES
(A) INDUSTRIAL
(B) MUNICIPAL
(C) BIOLOGICAL SYNTHESIS
(D) CHEMICAL
GENERAL CHARACTERISTICS
SPECIFIC GRAVITY
MLSS
MLVSS
SVI
SETTLING VELOCITY
SPECIFIC RESISTANCE
COEFFICIENT OF COMPRESSIBILITY
INORGANIC
ORGANIC
CHEMICAL ANALYSIS
Heavy Metals
Alkaline Earth Metals
Halogens
Nitrogen & Phosphorus
CALORIFIC CONTENT (Btu / lb VSS)
mg COD, TOC, TOD / mg VSS
NON-BIOLOGICAL & BIOLOGICAL - NON - ACTIVE
NON-BIOLOGICAL
BIOLOGICAL (Active)
Carbohydrates & Lignin
Alcohol Soluble
Alcohol Insoluble
Oil & Grease (Ether Extractables)
TTC (μ moles TF / mg VSS)
mg BOD / mg VSS
Oxygen Uptake (mg O2/hr / mg VSS) aerobic
DNA Conc / mg VSS
Plate Count (no cells / mg VSS)
Gas Production (vol produced / lb VSS) anaerobic

FIGURE 34

ANALYSIS FOR SLUDGE CHARACTERIZATION

## Aerobic Digestion

### Description of Process

Aerobic digestion is a process in which excess biological sludge is aerated for long periods of time, resulting in the cellular oxidation or destruction of volatile solids. The concepts of this destruction are similar to those applied in the extended aeration process, although the sludge age values are such that a less viable and more inert sludge is prevalent.

If the bacterial cells are represented by the chemical formula $C_5H_7NO_2$, then the cellular destruction through aerobic digestion is represented by: $C_5H_7NO_2 + 5O_2 \longrightarrow 5CO_2 + 2H_2O + NH_3$. This occurs when substrate in an aerobic system is insufficient for synthesis of energy, and the rate of destruction exceeds that of growth. Primary sludges often are combined with excess activated sludge, although the VSS destruction rate usually decreases as higher food to microorganism ratios (F/M) prevail.

### Design Considerations and Process Variables

1. nature and concentration of solids
2. solids loading
3. sludge age
4. oxygen and mixing requirements
5. environmental conditions (temperature, pH, *etc.*)

### Preliminary Investigation Requirements

The applicability of digesting sludges aerobically will depend on the nature of the sludge, the applied loading, and the sludge age. If aerobic digestion is considered as a candidate process in a waste treatment system, bench or pilot scale tests should be undertaken to determine the VSS destruction rates and oxygen requirements necessary for design purposes.

The destruction rates of digestible sludges can be evaluated in the laboratory using batch reactors such as those shown in Figure 22. The sludge mixture is aerated and the VSS measured at various periods of time. Once the VSS concentration becomes stabilized, the degradable fraction can be estimated. The data are then plotted and the empirical relationship determined.

The oxygen uptake rate of the sludge mixture is also monitored throughout the aeration period. This rate at the aeration time required for the desired VSS destruction level can then be used in estimating the system oxygen requirements.

## Anaerobic Digestion

### Description of Process

The anaerobic treatment of wastewaters of digestion of sludges involves a multitude of sequential biochemical reactions whereby facultative and anaerobic microorganisms ultimately convert organic material to carbon dioxide and methane. These reactions basically involve the conversion of substances such as organics, nitrates, and sulfates to reduced organics, carbon dioxide, methane, ammonia, and hydrogen sulfide.

As the anaerobic conversion of various substrate materials yields little energy to the microorganisms, only a small portion of the waste is converted to new cells. This is an inherent advantage of the anaerobic process in treating wastewaters, as large volumes of sludge are not synthesized as in the aerobic process. Other advantages include low nutrient requirements, no oxygen requirements, and production of a useful product, methane.

### Design Considerations and Process Variables

1. organic loading
2. solids loading
3. temperature and pH
4. acidity/alkalinity
5. hydraulic detention time and microbial growth rate
6. gas production
7. mixing
8. nature and concentration of solids

### Preliminary Investigation Requirements

Anaerobic digestion and anaerobic treatment of liquid wastewaters can be evaluated using bench scale units such as those shown in Figures 35 and 36 or on a larger pilot scale.

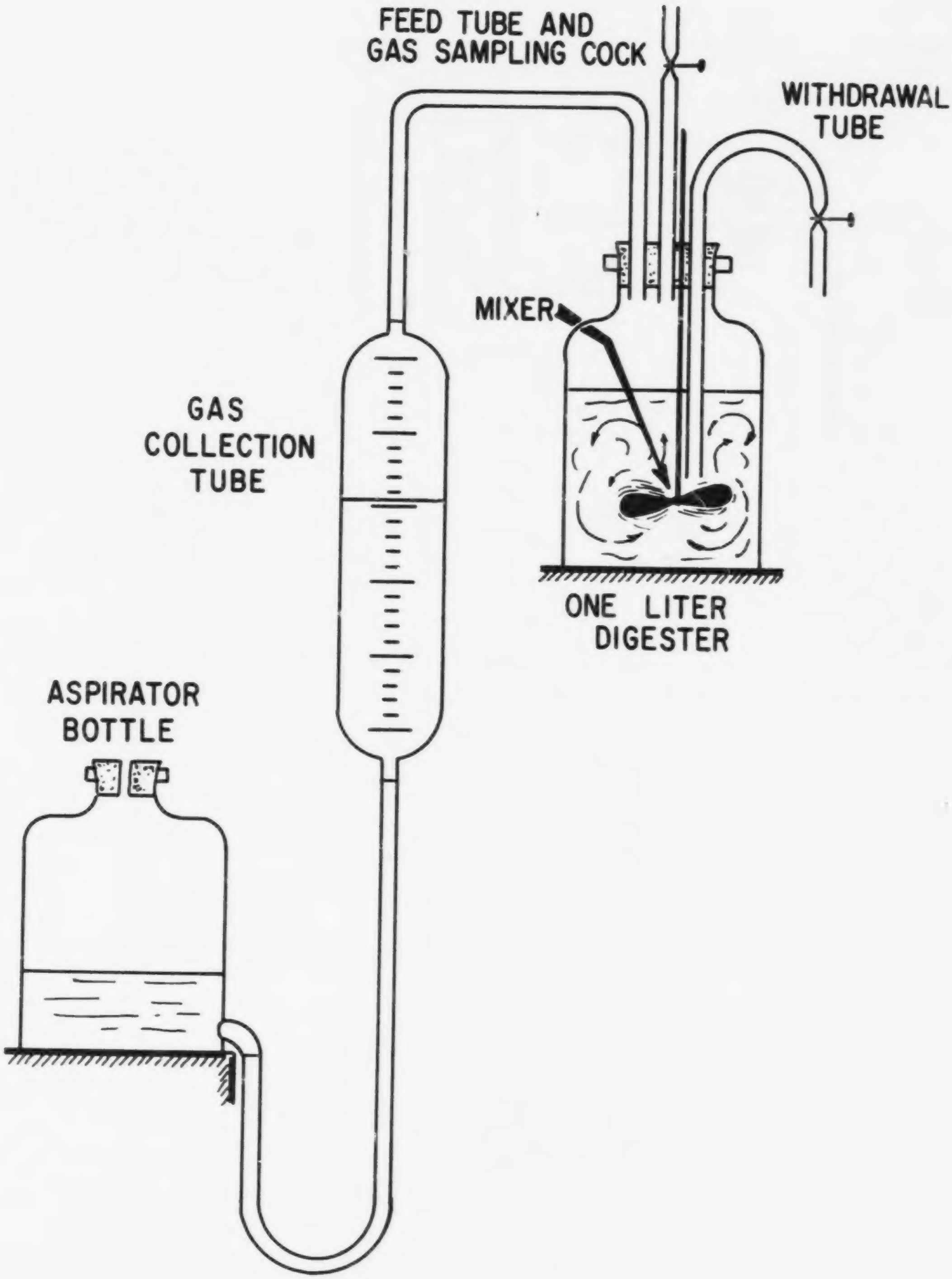
FEED TUBE AND
GAS SAMPLING COCK
WITHDRAWAL
TUBE
MIXER
GAS
COLLECTION
TUBE
ONE LITER
DIGESTER
ASPIRATOR
BOTTLE

FIGURE 35
LABORATORY BATCH-FED DIGESTOR

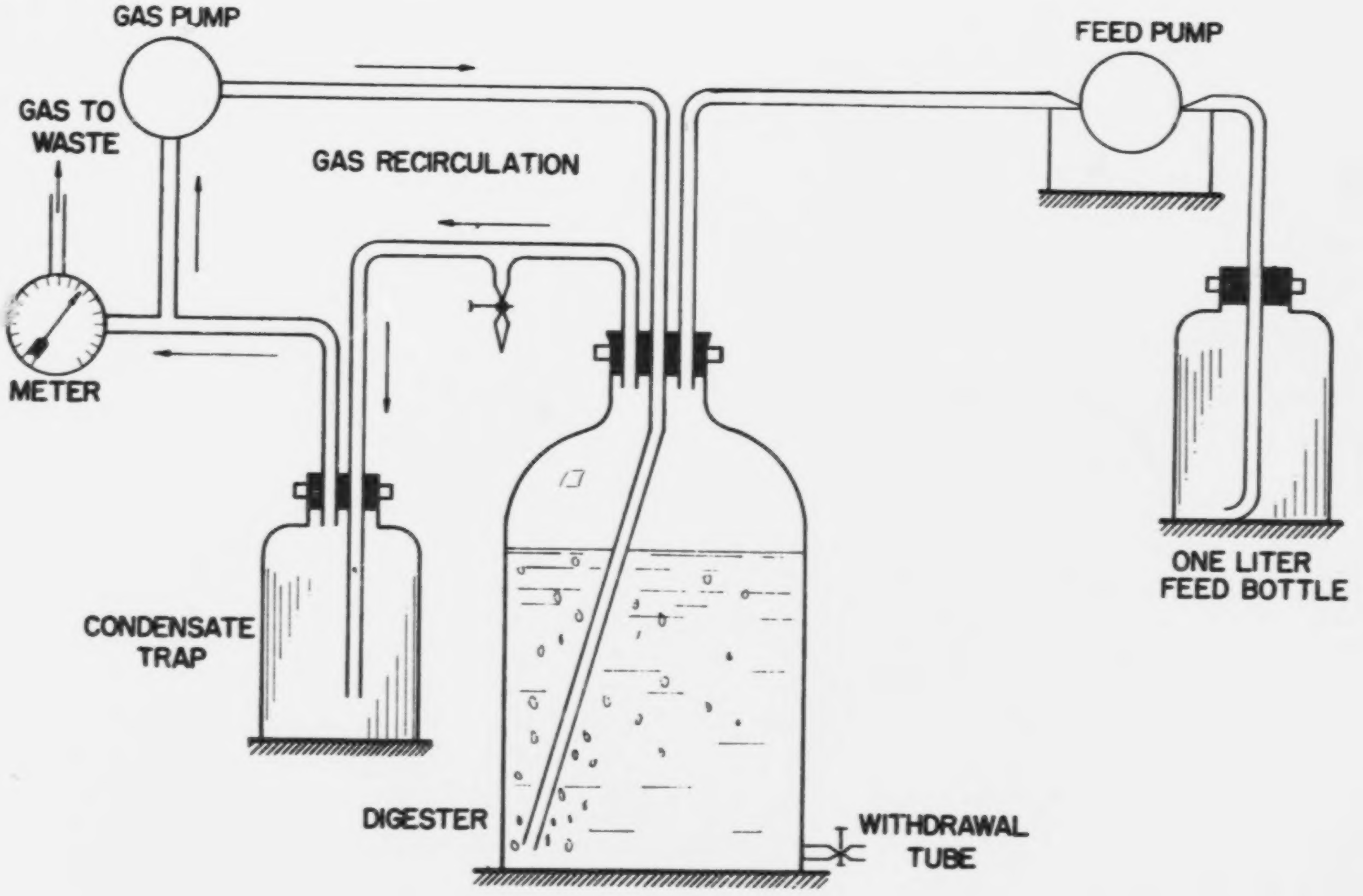
GAS PUMP
FEED PUMP
GAS TO
WASTE
GAS RECIRCULATION
METER
CONDENSATE
TRAP
ONE LITER
FEED BOTTLE
DIGESTER
WITHDRAWAL
TUBE

FIGURE 36

CONTINUOUS-FEED DIGESTOR

The process conditions can be changed as required in order to evaluate the corresponding process efficiency. It should be recognized that operation and control becomes time consuming and critical as the scale is increased.

## Heat Treatment of Sludge

### Description of Process

Heat treatment may be classified as a combustion process. However, much lower temperatures are used in heat treatment than used in the incineration process. The process may be expressed in terms of a "pressure cooker system" and is known as wet air oxidation. The process developed in Europe is known as the "Porteous Process" and the American version developed by Zimmerman is appropriately referred to as the "Zimmerman Process." In both methods the feed sludge temperature is elevated by passage through a heat exchanger and then the sludge is pumped to the reactor where steam is added. The reactor temperature is maintained at approximately 380$^{o}$F. The wet air oxidation process differs from the Porteous because of the addition of air and scrubbing of exhaust gases in the former. Both systems require that the sludge be ground to about .25-inch size particles and be pumpable.

Exposing the sludge to heat and pressure coagulates the solids, breaks down the gel structure, and reduces the hydration and hydrophilic nature of the solids. The liquid portion of the sludge can then be separated for additional dewatering and final disposal. Treating sludge, on leaving the reactor, passes through the heat exchanger, giving up most of its heat to the incoming raw sludge. After leaving the exchanger, the supernatant is decanted from the solids. The thickened sludge is dewatered further by one or more of several methods (Porteous,1968). Heat-treated sludge may be dewatered by filter presses or vacuum filters or used for landfill.

The Zimmerman Process has effectively treated sludges containing three to six percent solids without preliminary dewatering; however, economics seem to justify prethickening.

### Design Considerations and Process Variables

1. sludge flow
2. solids concentration
3. volatile solids concentration
4. chemical oxygen demand

5. chemical efficiency, COD removal
6. power recovery desired
7. sludge variability
8. ultimate disposal method
9. nature and composition of sludge

### Preliminary Investigation Requirements

The basic design criteria for heat treatment may be determined by performing physical and chemical analyses of the sludge. In a study covered by the United States Public Health Service ("Ultimate Disposal for Advance Waste Treatment AWTR-3"), it was concluded that data obtained from pilot plant studies were not amenable to simple kinetics and relations should be developed empirically for specific situations.

## Thickening

### Description of Process

Sludges from primary or secondary processes usually require thickening prior to dewatering by air drying, vacuum filtration, or centrifugation. If a sludge can be thickened, the process offers the advantages of improving digester operation, reducing sludge volumes for direct land or sea disposal, and enhancing the efficiency of process sludge dewatering systems.

Biological sludges usually can be thickened to a solids concentration of 4 to 6 percent, depending on the type of thickener and the nature of the sludge. As the ability of many sludges to thicken can be defined only in general terms, bench or pilot thickening studies should be initiated prior to finalizing the thickener design. Air flotation, mentioned previously, is also used for sludge thickening in certain applications.

### Design Considerations and Process Variables

1. sludge loading
2. diameter and configuration of thickening unit
3. depth of thickener

4. temperature

5. raking mechanism

6. detention time

7. sludge depth in thickener

8. general sludge characteristics

### Preliminary Investigation Requirements

The most common approach in evaluating thickening requirements for sludges is to use batch settling cylinders such as the one shown in Figure 20.

The sludge in question is put into the batch settling cylinder and the settling and thickening characteristics are evaluated under quiescent conditions, serving as the basis for scale-up and design (Eckenfelder and Ford, 1970; Edde and Eckenfelder, 1967).

## Lagooning

### Description of Process

Lagoons may be divided into 3 classes: (a) thickening, storage, and digestion lagoons; (b) drying lagoons; and (c) permanent lagoons ("A Study of Sludge Handling and Disposal", 1968).

Lagooning is the most popular sludge disposal technique at industrial wastewater treatment plants. Lagooning may be considered as a stage process in the handling of sludge or as a final sludge disposal process. The first type of lagoon is used when conventional digestion units are overloaded or sometimes as substitutes for conventional processes. Drying lagoons are used as substitutes for sand drying beds and a permanent lagoon where sludge is never removed is one of the cheapest methods of sludge disposal.

Permanent lagoons may be considered as a land filling method of sludge disposal. A supernatant decanting system enhances the operation of permanent lagoons by providing additional storage. Sludge stored in lagoons may be dewatered from about 95 percent moisture to 55 or 60 percent moisture in 2 to 3-year periods. The standard operating procedure for permanent lagoons is to discharge digested sludge to the lagoons at regular intervals, allowing a drying and cleaning period.

Waste stabilization ponds can be used effectively to treat excess activated sludge (Gloyna and Fisher, 1965). Lagoons are often used for sludge dewatering prior to ultimate disposal and in effect the lagoon acts as a gravity thickener. When a lagoon is used for dewatering and not permanent storage, recommended filling depths are 2.5 to 4 feet. However, ponds 5 to 6 feet in depth have been used to stabilize waste activated sludge.

### Design Considerations and Process Variables

1. available land area
2. climatic and atmospheric conditions
3. subsoil permeability
4. lagoon depth
5. lagoon surface loading
6. sludge characteristics
7. moisture content of sludge

### Preliminary Investigation Requirements

Sludge lagoons have been designed on the basis of surface or volumetric loadings or based upon ultimate disposal requirements. Model ponds illustrated in Figure 27 have proven useful in evaluating several variables of pond design. These model ponds were developed for studies of waste stabilization pond treatment of wastewaters, but can also be used to study sludge stabilization. Development of design criteria is dependent on lagoon type, *e.g.*, whether the process is to be designed for thickening, drying, digestion or storage.

## Sludge Drying Beds

### Description of Process

Dewatering of digested sludge is commonly accomplished by the use of open sand drying beds (Quon and Johnson, 1966). Sewage sludge should be properly digested before application to atmospheric drying as digestion enhances sludge drainability and raw sludge may cause undesirable odors (Jennett and Santry, 1969). Most beds are open and completely exposed, while others are glass-covered to reduce the effects of inclement weather on the drying process.

Drying beds usually consist of 4 to 9 inches of sand over 8 to 18 inches of graded gravel or stone. Six to 12 inches of digested sludge are applied to the bed and allowed to drain through the sand beds where the filtrate is collected by underground laterals, conveyed to sumps, and subsequently recycled through the plant. Experiments have shown that tile-drained sludge beds dry 25 percent faster than beds with impervious bottoms. However, other experiments and studies indicate that non-underdrained beds can be built and operated at one-fifth the cost of a tile-drained bed.

The sludge drying process incorporates drainage of the sludge moisture through the bed and the simultaneous removal of water by evaporation. The amount of moisture lost by evaporation during the initial stages is insignificant but becomes very important 1 to 2 days after the sludge is applied to the bed.

The sludge is allowed to dry until it reaches a "liftable" condition at which time the dried sludge is removed from the beds for final disposal. This condition normally occurs when the moisture content is 70-80 percent. The moisture content of the dried sludge is on the order of 60 percent.

Design Considerations and Process Variables

1. climatic and atmospheric conditions
2. depth of sludge application
3. presence or absence of chemical conditioning
4. sludge moisture content
5. source and type of sludge
6. extent of sludge digestion
7. sludge age
8. sludge composition
9. solids concentration when applied
10. sludge bed construction

### Preliminary Investigation Requirements

Only recently have attempts been made to formulate rational design standards for sludge drying beds. In the past, bed requirements have been based only on empirical relationships or experience factors.

Investigators have attempted to derive design criteria from laboratory experiements and pilot plant operations (Randall and Koch, 1969). However, correlation between experimental data and actual plant data has been relatively poor.

Selected variables of the sludge drying processes have been successfully studied in the laboratory as well as on a pilot plant scale (Carnes, 1966). Experimental units have also been useful for evaluating the effects of chemical conditioning on sludge drying.

## Vacuum Filtration

### Description of Process

Vacuum filtration is used to dewater wastewater sludges in which water is removed under an applied vacuum through a porous media which retains the solids. In the operation of vacuum filters, a rotary drum passes through a slurry tank in which solids are retained on the drum under an applied vacuum. When the drum emerges from the slurry tank, the deposited cake is further dried by the transfer of liquid to the air which is drawn through the cake by the applied vacuum. The filter cake is then removed to a collection hopper for hauling or incineration.

### Design Considerations and Process Variables

1. sludge feed concentration
2. sludge conditioning (chemical additives)
3. degree of thickening preceding filtration
4. sludge viscosity
5. filtrate viscosity
6. operating vacuum
7. chemical and physical composition including partial size, shape, *etc*.
8. type and porosity of filter media

### Preliminary Investigation Requirements

The most rapid means of estimating the vacuum filter yield for a given sludge is by use of the leaf test apparatus. The test variables such as an applied vacuum, sludge concentration, sludge conditioning, etc., are established and the sludge yield for each condition is estimated (Eckenfelder and Ford, 1970). Continuous pilot scale tests are recommended if design information for large and costly vacuum filtration installation is required.

## Centrifugation

### Description of Process

Basically, centrifuges separate solids from the liquid through sedimentation and centrifugal force. The most effective centrifuges for dewatering sewage sludges are horizontal, cylindrical-conical, solid bowl machines ("A Study of Sludge Handling and Disposal", 1968).

In a typical unit, sludge is fed through a stationary feed tube along the center line of the bowl to the hub of the screw conveyor. The screw conveyor is mounted inside the rotating conical bowl and rotates at a slightly lower speed than the bowl. Sludge leaves the end of the feed tube, is accelerated, passed through the ports of the conveyor shaft, and is distributed to the periphery of the bowl. The solids are settled through the liquid and are moved along the bowl wall by the blades of the screw conveyor. The solids move out of the liquid bowl and onto a drainage deck on which they are continuously conveyed by a screw to the end of the machine, at which point they are discharged. The liquid effluent is discharged through effluent ports after traveling the length of the pool under centrifugal force. The depth of the liquid or pool volume can be varied by adjustment of weir plates located at opposite ends of the bowl.

Centrifugation has been used for sludge thickening and sludge dewatering, and has been used with and without chemical conditioning or the addition of polyelectrolytes. The centrifuge is most effective in recovering primary solids, and least effective when recovering waste-activated sludge.

### Design Considerations and Process Variables

1. feed rate
2. sludge solids characteristics
3. feed consistency

4. temperature
5. chemical additives
6. bowl design
7. bowl speed
8. pool volume
9. conveyor speed

### Preliminary Investigation Requirements

Unlike filtration, it is not easy to predict centrifugal performance by the use of laboratory techniques. Pilot studies must be made and appropriate scaling factors determined for process design. When scaling pilot plant data to larger units, it is necessary to consider the residence time of the liquid in the bowl, the solids thickness and the residence time of the solids on the beach, and particularly the effective centrifugal force on the liquids and solids (Albertson and Guidi, 1969).

It may be possible to determine the feasibility of centrifugation from simple laboratory tests. The sludge to be dewatered may be spun in a laboratory hand centrifuge for 30 seconds at 2,000 rpm, and after centrifugation, the tube filtered to determine the stability of the deposited cake.

## Filter Press

### Description of Process

Filter pressing presently is not widely practiced in the United States, probably because of the high labor and maintenance costs involved in the batch operation. However, the applicability of filter pressing sludges is becoming more promising. The press does not dewater solids by squeezing, but rather acts as a pressure filter similar to a rotary vacuum filter with the exception that higher pressures are used. Like the vacuum filter, the filter press usually requires chemical conditioning, bench scale filtration studies, and careful selection of the filtering media. Economics of the process dictate sludge concentrating by some other means prior to pressing.

The "Sludge All System" developed by Beloit-Passavant Corporation is a completely automated process and the customary shutdown for cake removal is not necessary. The system includes thickening, pressing, and incineration; and the accumulated filter cake from the press contains about 50 percent solids.

Thickened sludge is ground prior to filtration and often a precoat is added and mixed with the feed sludge before pressing. The sludge enters the press through a center feed and is forced into the filter modules. The filtrate is continuously pressed through the fabric and discharged for recycle.

### Design Considerations and Process Variables

1. sludge volumes
2. raw sludge solids concentration
3. nature of the sludge
4. chemical conditioning
5. ultimate disposal of filter cakes
6. filter pressing pressure
7. filter mesh aperture size
8. filter pressing time

### Preliminary Investigation Requirements

The basic design criteria for sizing a filter press unit can be developed by use of a pilot plant unit. Pilot plant data should also provide thickening and chemical conditioning requirements. Means for ultimate disposal of the cake solids often will dictate the required solids concentration in the final sludge cake. A final cake solids of 40 percent may be expected in the sludge cake provided feed solids are maintained near 10 percent.

## Land Disposal

### Description of Process

The disposal of liquid digested sludge on open land surfaces is quite common among smaller wastewater treatment plants. In England, the disposal of liquid sludge to farmland is very popular and in the arid and semi-arid parts of the United States, the reclamation of water from municipal sewage is becoming increasingly recognized as an important water conservation measure. Liquid digested sludge and supernatant have been applied to lands for final disposal to fertilize grass or agricultural crops for soil conditioning. Digestion, aerobic or anaerobic, is almost always required before spreading liquid sludge on land. Sludge is distributed on the land and processed in a variety of ways. The sludge may be injected into the subsoil under pressure or simply pumped or gravity fed through a pipeline to agricultural fields or land to be reclaimed. A common technique is disposal directly to the land by spraying from tank wagons.

### Design Considerations and Process Variables

1. proximity of surface waters and distance to groundwater table
2. toxic constituents of the sludge
3. nutritional value of the sludge
4. availability of disposal sites
5. transportation costs
6. suitability of soil for sludge disposal
7. nature of any aesthetic nuisance
8. effects on vegetation
9. application rates
10. atmospheric and climatic conditions
11. method of sludge application

### Preliminary Investigation Requirements

Design criteria can only be developed through the use of fairly large demonstration sites and extensive time involving studies is required. The effects of land disposal on crops and ground and surface waters is of paramount importance (Sosewitz and Hinsly, 1969).

## Sludge Incineration

### Description of Process

Various incineration processes have been applied to the disposal of residues resulting from wastewater treatment. These processes may be classified as multiple hearth fluidized bed flash combustion and atomized suspension. The wet oxidation process (classified previously under heat treatment) and incineration are considered combustion processes. All these methods depend to some extent on the organic material in the waste as a source of fuel. However, regardless of the heat value of the sludge, some axuiliary fuel system is necessary during start-up of the incineration process. The incinerator may be classified as an open flame water evaporator since the actual incineration does not take place until the sludge has lost most of its moisture through evaporation (Sparr, 1968). The temperature in the burning zone must be at least 1,350 to 1,400° F for complete combustion of the sludge solids and for complete oxidation of the existing gases to innocuous compounds.

In the multiple hearth furnace, preconditioned dewatered sludge is conveyed to the upper hearth of the furnace, and mechanical rakes move the sludge from one hearth to the next lower hearth, where the sludge is sequentially dried, burned, and the ashes cooled.

In the fluidized bed incinerators, air is utilized to maintain hot sand in an expanded or fluidized state. The violent boiling of the expanded sand allows intimate contact of the sludge and other fuel with oxygen without the aid of mechanical mixing. Dewatered sludge is fed directly into the fluidized bed to which preheated air is introduced.

The atomized suspension process is essentially a high-temperature, low-pressure thermal process for the oxidation of fine particles of sludge to innocuous ash. Sludge is concentrated, ground, and sprayed as an atomized suspension into a stainless steel cylinder. The walls of the cylinder are maintained at a temperature between 1,000 to 2,000°F and heat is transferred to the falling droplets of sludge by radiation. In the cyclone flash dryer and incinerator process, dewatered sludge is mixed with previously heat-dried sludge to produce a fluffy material. In this form, it is carried through the drying stage by the high velocity of hot gases and the dried sludge is burned in the furnace.

## Design Considerations and Process Variables

1. sludge flow
2. moisture content of sludge
3. volatile solids content of the sludge
4. heat value of the sludge
5. type of operation, continuous or intermittent
6. source and type of auxiliary fuel
7. method of final disposal of solid residue
8. sludge variability
9. sludge loading
10. possibility of alternate methods

## Preliminary Investigation Requirements

Design criteria are established through incinerating the sludge in a bench or pilot scale burner. The auxiliary fuel requirements, nature of the ash, and composition of the off-gases are the important parameters to be ascertained.

## Transportation of Sludge and Sea Disposal

### Description of Process

Sludge may be transported by rail, truck, barge, pipe, or conveyor. For hauls up to 50 miles, it is likely that truck transportation would be more economical than rail. Freight rate structures in the United States are extremely diverse, causing comparisons of transportation methods to be difficult at best. In addition to the cost of hauling, there will be an incurred cost for loading sludge into hopper cars in the case of rail haul or pumping sludges to barges in the case of barge haul. Barge rates are lower than rail rates since the tractive force involved is less and barging normally does not bear the cost of the waterway.

For coastal communities or communities adjacent to the well-developed inland waterway systems on the Mississippi, Ohio, Missouri, Illinois, and Tennessee Rivers, sea disposal is frequently the most economical and simplest method available for ultimate sludge disposal, although this entire concept is presently under review by the regulatory agencies. It should be recognized that present and future laws governing sea disposal practice will in large measure dictate its economics.

### Design Consideration and Process Variables

1. proximity of final disposal site
2. pretreatment required
3. transportation unit costs
4. type of transportation available
5. distance to loading point
6. requirements for final disposal
7. sludge characteristics

### Preliminary Investigation Requirements

The decision to use transportation in conjunction with sludge disposal is based upon an analysis of alternate dewatering and disposal methods. Laboratory analyses of the sludge are required for such an investigation. There are many factors that may rule out the possibility of sludge transportation, such as the unavailability of economical transportation or the distance to a final disposal site. Barging and sea disposal should be considered as a means for ultimate sludge disposal for plants located near rivers close to the sea.

## ULTIMATE DISPOSAL

The final disposition of residual or refractory wastewaters and sludges resulting from various processes is generally termed "ultimate disposal."

Solutions to ultimate disposal problems include subsurface storage, conversion of wastes to innocuous end products, storage in ponds or land spreading, and ocean disposal. Land spreading, lagooning, and ocean disposal processes have been presented elsewhere and only deep well injection and thermal oxidation are discussed herein. These processes are further described in terms of their treatability or preliminary investigation requirements.

### Thermal Oxidation

#### Description of Process

The thermal oxidation of liquid wastewaters involves the transfer of heat from an auxiliary fuel to the wastewater. In some cases, the wastewater has calorific value which decreases the total auxiliary fuel requirements.

The wastewater is first atomized as finely as possible in order to present the greatest surface area for mixing with combustion air. The temperature of the system is maintained at a level necessary for the reaction to proceed and sufficient residence time is provided to allow complete oxidation. The system is also designed so that there is sufficient turbulence for air, liquid, and fire contact.

The equipment normally consists of a horizontal or vertical refractory lined furnace with an auxiliary fuel burner firing at one end or tangential to a cylindrical shell. The size of the incinerator depends on the heat release of the system, the amount of combustion air to be used, and the quantity of wastewater injected.

#### Design Considerations and Process Variables

1. flow
2. calorific value
3. residence time in burner
4. air flow
5. ignition temperature of organic material in the wastewater
6. degree of wastewater atomization

7. degree of system turbulence

8. auxiliary fuel calorific value

### Preliminary Investigation Requirements

Before any liquid incineration unit is installed, pilot scale studies should be undertaken. This requires that representative samples either be obtained from the waste stream or synthesized. The wastewater is then fed to the pilot liquid incineration unit, atomized, and burned. The stack gases are monitored for products of incomplete combustion while process variables such as auxiliary fuel feed, wastewater pumping rates, temperatures, etc., are varied as required throughout the test series. The necessary design criteria then can be established based on observed performance.

## Deep Well Disposal

### Description of Process

Subsurface disposal of liquid wastes is not a new concept as the oil and gas producers have been using this method for disposal of oil field brines for half a century. Only recently have the process industries realized the applicability of deep well injection for disposing of concentrated and relatively untreatable waste streams. The depth at which these wastes are discharged vary from a few hundred feet to over 2,000 feet and well head injection pressures for some wells have approached 4,000 psi (Gloyna and Ford).

A suitable disposal formation is the very heart of a good disposal system and if water can be disposed of with a vacuum on the injection well head, operating expenses would be much less than when injection pressures are required (API, 1960).

Deep well disposal requires the injection of liquid waste into a porous subsurface stratum which contains noncommercial brines. The wastes are merely stored below ground in strata which are sealed by impervious strata, thus isolated from usable underground water supplies or mineral resources. The disposal system consists of a well and surface equipment, such as pumps and pretreatment units.

### Design Considerations and Process Variables

1. subsurface geology
    a. permeability
    b. porosity
    c. fracture gradient

2. subsurface hydrology
3. fluid compatability
4. pretreatment considerations
5. flow
6. characteristics of waste, including temperature

Preliminary Investigation Requirements

Initially, a feasibility study is required which includes acquisition of basic information concerning subsurface geology and hydrology. Based on these data, the operating well head pressure may be estimated and for steady-state single-phase flow, the injection rate may be predicted. Pilot wells are often constructed prior to the design and construction of the waste injection well system. Preliminary estimates of injection rates and hole pressure may be verified by these pilot studies. These studies are particularly important for the design of wastewater pumps and appurtenances. The test hold will also serve to identify subsurface geology and allow for sampling of the formation fluids. The duplication of formation hydrologic and geologic conditions in the laboratory is highly impractical and in most cases impossible.

Fluid compatability can be evaluated in the laboratory by mixing the waste and formation waters and observing any changes in the physical appearance. Preliminary investigations should also include bacteriological analyses of the formation water and wastewater as microorganisms may also cause plugging of the well formation.

## COMPARISON OF LABORATORY AND PROTOTYPE TREATABILITY INFORMATION

It is important to know the aspects of using laboratory data for the design of prototype units. Adjustment of laboratory data to prototype units is often accomplished by the application of "scale-up" factors which take into account the uncertainties involved in the process operation and the variable environmental conditions. Factors which should be considered in determining the scale-up factors will be discussed herein.

Biological reactions can be considered to be unaffected by the size of the unit (Eckenfelder and Cardenas, 1966). The biological mass (MLVSS) requires the same amount of oxygen to decompose a unit weight of contaminants in a BOD bottle as it will in a one million gallon aeration tank, and the degradation of contaminants per unit area of trickling filter slime will have the same potential activity regardless of the size of the unit. The quantity of chemical additives per unit volume of waste required to cause effective coagulation will be the same whether the reaction occurs in a one liter jar or in the actual industrial treatment plant. However, in all of these particular cases, the desired reaction occurs only if the required reaction components are thoroughly mixed for the required length of time.

The formation of hydrous microflocs during the initial rapid mix phase of coagulation occurs in the first 0.1 seconds (Reddick, 1968), but the actual design detention time for flash or rapid mixing is on the order of 30 seconds. The difference between reaction time as determined in the laboratory and the design time may be attributed to difficulties in dispersing the chemicals in a large volume of wastewater and the probability of the coagulant entering into undesired side reactions.

The more significant problems which must be considered in applying laboratory treatability information to the design of prototype units is summarized in Table 19. Sources of scale-up problems may be categorized under (1) process considerations, (2) selected wastewater characteristics, and (3) environmental factors. Perhaps the most important process consideration is that of providing complete mixing in each process unit for the designed length of time. One investigator doubts whether more than 70 percent of a wastewater will remain in a treatment unit for the designed length of time when the detention period is based on the volume of flow and the unit volume (Weber, 1969). Other studies have indicated that a maximum of 50 percent flow remains at $t = V/Q$ in long narrow tanks. Recently completed flow studies at the Deepwater Pilot Plant in New Jersey, sponsored by the Delaware River Basin Commission, participant industries, and the Environmental Protection Agency (EPA) indicated the relative amounts of perfect mixing, plug flow, and dead space that was occurring in each unit process using dye tracers. The method applied proved to be very effective in evaluating the hydraulic characteristics of the neutralization tanks, reactor clarifier, aeration basins, and the secondary clarifier (Wolf & Resnick, 1963).

Although residence time is one factor which relates bench scale and prototype responses, turbulence or "mixing intensity" is another

## TABLE 19

## TREATABILITY PROBLEMS LEADING TO SCALE-UP FACTOR CONSIDERATIONS

I. PROCESS

  A. Hydraulic Considerations - Short Circuiting in Completely Mixed Systems

  B. Inadequate Aeration in Aerobic Processes

  C. Insufficient Contact of the Decomposing Media with Wastewaters

  D. Adequate Dispersion of Chemical Additives

II. WASTE

  A. Wastewater Variability

    1. Flow

    2. Chemical Contaminants (Organic and Inorganic)

    3. Physical Contaminants

    4. Temperature

  B. Presence of Toxic Materials - Toxic Threshold

III. ENVIRONMENTAL

  Temperature Surroundings

  Possibility of Critical Plant Unit Failures one that has yet to be explicitly defined. Until significant parameters characterizing turbulence can be developed, there will be certain unknowns involved in translating bench scale data to full-scale design criteria. The expected variations in wastewater flow and composition must be taken into consideration so that the treated effluent will be acceptable for subsequent treatment and/or discharge into receiving waters. Finally, the application of treatability results obtained under constant laboratory conditions must be translated to one of varying environmental conditions. Process operating characteristics obtained from studies conducted at a constant 20°C will be very different when subjected to temperatures as high as 35°C, which is common in the Southwest United States; or temperatures as low as -40°C, which are common in the Northern United States, and commonly applied temperature correction factors may or may not be applicable.

Very little information on comparisons of operating prototype and laboratory units is available. However, the results of several investigations indicate that laboratory treatability studies produce valid and applicable information which may be translated into design criteria for prototype units (Ford and Eckenfelder, 1966). Ford and Eckenfelder (1966) compared the operating characteristics of laboratory scale continuous activated sludge units to prototype field units treating a petrochemical wastewater. The laboratory units had aeration compartment volumes varying from 36 to 9.6 liters; and the variables which were to be compared with the field data at various loadings included sludge volume index (SVI), oxygen uptake rate, bacterial activity (dehydrogenase enzyme test), settling velocity, and COD removal. The results of these comparisons indicated that the removal efficiencies were reasonably similar in the laboratory and prototype units operating in the activated sludge regime (Table 20). Information extrapolated from the laboratory units indicated that the oxygen uptake rate at a loading of 0.24 lbs BOD/day/lb MLSS would result in an oxygen uptake of about 8 mg $O_2$/hr/gm MLSS. The oxygen uptake rate measured in the prototype unit at this loading was 9 mg $O_2$/hr/gm MLSS.

An analysis of the bench and pilot scale data for a combined refinery and petrochemical waste showed a similar correlation. The two units were operated nonconsecutively at a loading of 0.24 (lb BOD/day/lb MLVSS). The bench scale continuous units, operating with an aeration chamber volume of six liters showed an average BOD removal of 97 percent, with an average oxygen uptake rate of 10.4 mg $O_2$/hr/gm MLVSS. The pilot scale unit, operating under similar environmental conditions with an aeration chamber volume of 54,400 gallons, exhibited a BOD removal of 89 percent and an average oxygen uptake rate of 7.2 mg $O_2$/hr/gm MLVSS. The lower efficiency of removal for the pilot plant can be attributed to operational difficulties as well as batch dumps of inhibitory substances within the refinery & petrochemical complex during this period of operation.

In any comparison between laboratory and pilot units, differences in operational efficiencies can be expected. Differences in the mixing intensities, fluctuating influent feed concentrations, hydraulic short-circuiting, and problems relating to sample collection can allude to poor correlation. Based on

## TABLE 20

## COMPARISON OF AVERAGE ACTIVATED SLUDGE OPERATIONAL VALUES FOR BENCH SCALE AND PROTOTYPE UNITS

(Eckenfelder and Ford, 1968)

| | $L_f$ $(\frac{\text{lbs BOD/day}}{\text{lb MLSS}})$ | SVI | Oxygen Uptake ($mgO_2$/hr/ gm MLSS) | Dehydrogenase Enzyme $(\frac{\text{moles}}{\text{mg VSS}})$ | COD Removal (%) | Zone Settling Velocity (ft/hr) |
|---|---|---|---|---|---|---|
| | 0.10 | 164 | 5 | .021 | 73 | 6.5 |
| | 0.17 | 96 | 6 | .023 | 72 | 14.5 |
| | 0.39 | 84 | 11 | .032 | 69 | 20.0 |
| | 0.40 | | 13 | .038 | 68 | |
| | 0.58 | 110 | 24 | .025 | 60 | 13.0 |
| | 0.83 | | 31 | .064 | 61 | |
| | 0.96 | 480 | 55 | .035 | 52 | .30 |
| | 1.60 | - | 65 | .060 | 54 | nil |
| | 2.30 | - | 78 | .105 | 50 | nil |
| Prototype Data | 0.24 | 130-150 | (9) | .023 | (78-84) | - |

NOTE: Temperature of Aeration Basin, Bench Scale Studies: 23°C
Temperature of Aeration Basin, Prototype: 34°C

this recent experience, the organic removal observed in pilot facilities is slightly less than that obtained in bench scale units. The magnitude of this difference will depend on the nature and "representativeness" of the wastewater, the degree of mixing, and operational factors.

## AERATION

The rate of oxygen transfer into wastewaters is one of the most important design considerations in all high rate aerobic biological treatment processes. At the present, there is no commonly accepted method for designing full-scale aeration units from data obtained on bench scale experiments. However, recent information indicates that at lease one approach would yield a scale-up method that would be applicable to all types of aeration processes. This approach involves determining both the mixing characteristics of an aeration device and the relationship between the overall oxygen transfer to a common substance such as tap water. The turbulence caused by an aeration device can be related to the characteristics of the liquid and the mixing device by the Mixing Reynolds Number. By definition this number is equal to the ratio of inertial forces to viscous forces (Mancy and Okum, 1965) and is expressed as follows:

$$N_{Re} = \frac{\text{inertial forces}}{\text{viscous forces}} = \frac{d^2Np}{v}$$

where:

$d$ = the length of the agitating mechanism

$N$ = the number of revolutions per unit time

$p$ = the liquid density

$v$ = the viscosity

Since various components of wastewaters affect the efficiency of oxygen transfer, it is necessary to relate the transfer capacity to a common factor. This has been done by using tap water and determining the $\alpha$ factor (Eckenfelder and Ford, 1968), which is the ratio of oxygen transferred in wastewater to the oxygen transferred under similar conditions in tap water, or:

$$\alpha = \frac{K_{La} \text{ of wastewater}}{K_{La} \text{ of tap water}}$$

By determining the mixing characteristics using the Mixing Reynolds Number and the relation between mixing and the oxygen transfer in both the tap water and the wastewater, it would theoretically be possible to design full scale units based on laboratory experiments with tap water. This approach remains to be developed.

## GRAVITY THICKENING

One of the most common methods of concentrating wastewater sludges is by the sedimentation process called gravity thickening. Laboratory development of data for the design of this unit is usually dependent upon simple batch settling tests performed in 1 liter graduate cylinders. It has always been accepted that this method is subject to a multitude of errors but that it was the only feasible approach. Edde and Eckenfelder (1967) studied the relationship between simple 1 liter batch settling tests and the operation of continuous prototype thickeners. A mathematical model was developed which related a constant (CD) to the initial sludge concentration, the underflow sludge concentration and the mass loading. The value of this constant was determined for several prototype continuous flow units ($CD_t$) and compared to the value obtained in the 1 liter batch settling tests ($D_b$). It was found that the ratio, $D_t/D_b$, was closely related to the sludge blanket depth in the prototype thickener. The relation between the ratio $D_t/D_b$ and the sludge depth is shown in Figure 37. The authors concluded that once $D_b$ is determined from bench scale batch settling curves the prototype operating Dt may be determined from the ratio of $D_t/D_b$.

## ACTIVATED CARBON ADSORPTION

Adsorption of organics on activated carbon is rapidly becoming one of the most successful advanced wastewater treatment processes, and in some instances represents a favorable economical alternative to biological treatment (Hager and Reilly, 1969; Zanitsch and Morand). Two bench scale methods are commonly employed to determine the design parameters for this process: 1) adsorption isotherm development tests, and 2) continuous flow column tests. Briefly, the isotherm method consists of a batch test where the adsorption capacity of a given type of activated carbon is determined by exposing a small measured weight of the carbon to a volume of between 100 and 500 ml of the wastewater. The columns are usually built on a large scale requiring several weeks of continuous operation and several thousand gallons of wastewater.

Because of the difficulty in constructing and operating columns, batch tests to determine adsorption isotherms are often employed. However, it has been concluded in some studies that adsorption isotherms are of little or no value in determining the organic carbon removing capacity for waste treatment applications. There are many specific problems inherent in scale-up of adsorption isotherms to prototype units. This method is useful when dealing with solutions containing only a few organic species. In most wastewaters there are many organic species and the concentration of these organics is constantly changing. The adsorption isotherm does not account for other mechanisms which remove organics from wastewaters in activated carbon filters. Factors such as biological

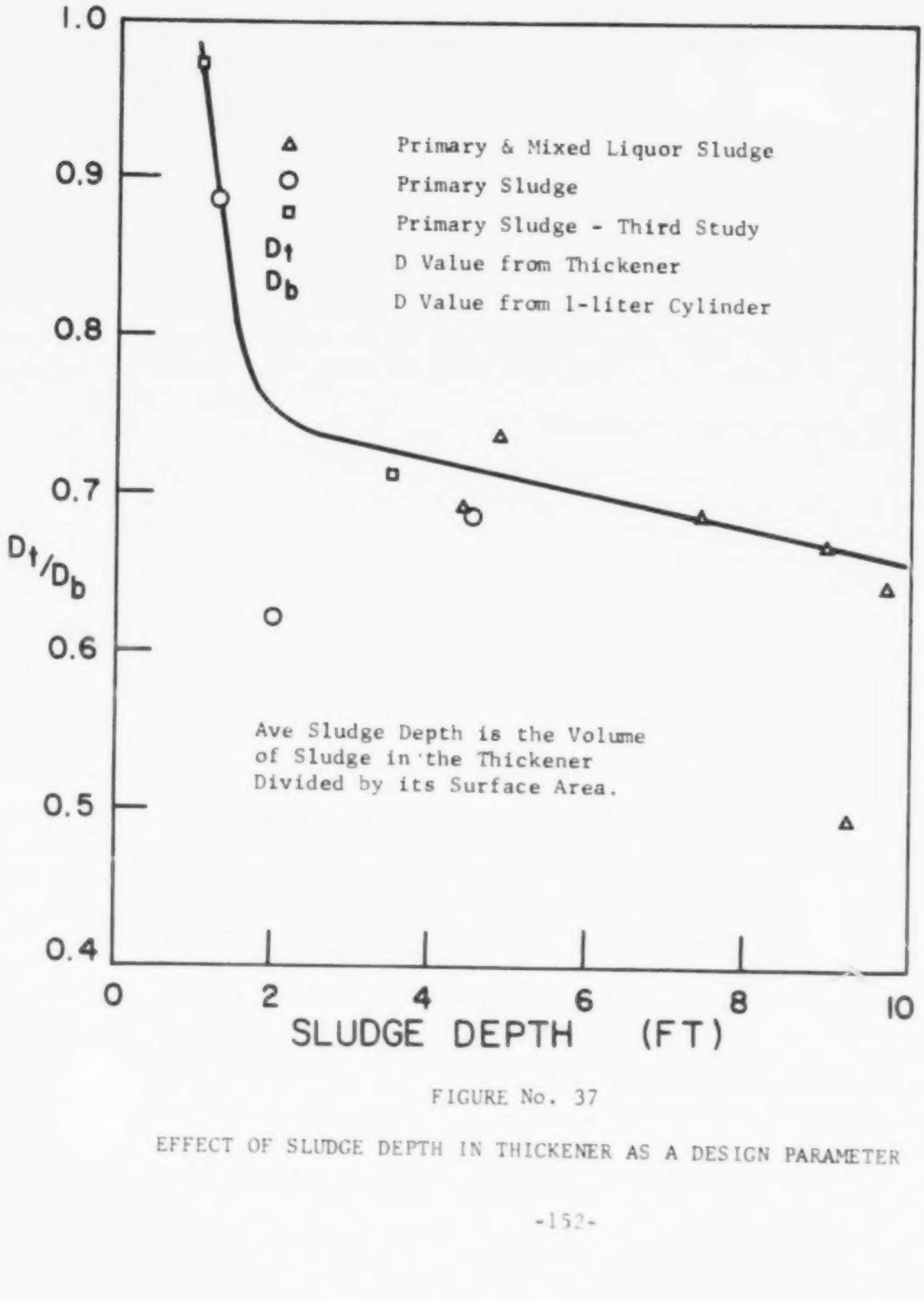

FIGURE No. 37

EFFECT OF SLUDGE DEPTH IN THICKENER AS A DESIGN PARAMETER activity in the carbon beds, filtration of suspended matter and blending of multiple bed effluents all tend to provide higher removals than would be indicated from adsorption isotherms derived from batch tests.

Thus, rather than applying a "scale-up" factor in adsorption studies, a "scale-down" factor must be used since bench scale tests generally underestimate prototype performance. Because of the dependence of adsorption on the size of the activated carbon, the characteristics of the wastewater studied, and other experimental conditions, it is impractical to determine a common scale-down factor that may be used for prototype design. However, the following example indicates the order of magnitude of scale-down when similar wastewaters are tested under similar conditions (Zanitsch and Morand). Small bench scale adsorption isotherms were used to study the removal of soluble organics from the effluent of a conventional activated sludge unit. Column studies were initiated at the plant site using 4 separate 4-inch diameter columns connected in series with a total depth of 18 feet. These columns were operated continuously for 31 days at an average flow of 320 gallons per day. A pilot plant of 0.3 mgd capacity was utilized to complete the comparative carbon adsorption studies. The plant was operated under loading conditions similar to those used in the column studies. Results of these investigations are reported below:

| | Method Utilized | Adsorption Capacity $\frac{\text{lb organic adsorbed}}{\text{100 lbs Activated Carbon}}$ |
|---|---|---|
| 1. | Bench scale batch analyses | 3 |
| 2. | Continuous flow columns | 14 |
| 3. | Prototype | 35 |

The prototype units were about 2.5 times more efficient as the continuous flow laboratory units. The "scale-down" factor in this case of laboratory batch scale to laboratory continuous scale to prototype unit was: 10:2.5:1; thus the importance of estimating these factors for each waste treatment situation is underscored.

## CHEMICAL COAGULATION

The results of one study showed pilot scale chemical coagulation units to be more effective than the larger prototype facility (Schindler, 1951). In this particular study, the pilot plant which was one-seventh the size of the prototype facility, was operated as a lime coagulation unit process for the removal of white oils and sulfonates from a refinery effluent. The 2 units were compared under similar loading conditions and the optimum lime dosages were 1.05 tons per 100,000 gallons and 0.7 tons per 100,000 gallons for the pilot and prototype plants respectively. In this case, the scale-down factor was equal to 0.7.

It is emphasized at this point that bench or pilot scale studies should be continuous reactor studies when the resultant data is to be translated into design criteria for continuous flow field units. Scale-up factors, such as they are, are easier to predict and their magnitudes are closer to unity and less fluctuative than those resulting from batch studies.

## MANPOWER AND TIME REQUIREMENTS

The implementation of water pollution control programs has not kept pace with modern technological developments for 2 reasons (U. S. Senate, 1969):

1. an effective system for forecasting the supply and demand of the various categories of operator, technician, and professional level personnel needed in the water pollution control effort has been lacking; and,

2. lack of the above system has resulted in a shortage of treatment plant operators and of training opportunities to improve the necessary skills.

There is no doubt that present technology has the potential for alleviating or eliminating many of the prevalent water pollution problems. Placing adequately trained personnel at key positions in pollution control programs is the most direct and efficient way of achieving increased pollution abatement. The manpower and time requirements for planning and executing wastewater surveys, wastewater characterization studies, in-plant improvements and treatability studies are summarized herein.

The time requirements and the quality of the personnel necessary to complete a treatability study for any given industry will vary widely with the size of the industry and the complexity of its wastewaters. Because of the diversity of the problem, very few data are available concerning the actual requirements of treatability studies. However, the skills and experience needed to conduct treatability studies are similar to those required of personnel charged with supervisory and/or operational responsibility for water pollution control facilities and information is available in these areas (Anon, 1968). A study was recently completed on the identification of the needs and problems of operational personnel responsible for operation of municipal and industrial wastewater treatment facilities. Particular attention was paid to the requirements necessary to perform specific task functions, and the total educational experience was related to the full time equivalents required to satisfactorily operate and maintain a treatment facility. The needs for task functions varying from those of operations, maintenance, evaluation, and supervision of treatment facilities were considered (Anon, 1968).

Treatment facilities surveyed in the time and qualifications study included operating petrochemical and refinery industries with the following treatment units:

| Pre or Preliminary | Secondary | Sludge Handling |
|---|---|---|
| API Separators | Deep well injection | Centrifugation |
| Neutralization | Filtration | Digestion |
| Equalization | Activated Sludge | Thickening |
| Coagulation-precipitation-sedimentation | Extended aeration | Filtration |
| | Waste Stabilization ponds | Landfill |
| | | Incineration |

The major responsibilities and time-consuming duties generally increase with the number of different unit processes and wastewater flows. These requirements for 4 industries are summarized in Table 21. The full time equivalents (FTE) represent the number of man days required to complete the task function per 8-hour shift. For example, if 1.5 FTE are required to complete a task, this means that a total of 12 man hours must be utilized during each 8-hour shift to satisfy this task function.

These personnel requirements were ascertained through personal communication and questionnaires with the industries cited. The industries were selected to represent a broad spectrum of treatment facilities, and the delineation of personnel requirements for primary and secondary treatment and sludge handling were based on extensive discussion concerning the allocation of operating time to each of the unit processes.

The various task functions and the education required for the operation of all wastewater abatement facilities are listed in Table 22. The task of planning and conducting treatability studies requires personnel with qualitifications equivalent to those listed under Area V of Table 22, while support personnel may be drawn from the remaining categories.

A meaningful wastewater study will be contingent upon the successful completion of the sequential process outlined in Figure 38. Many industries maintain a staff of consultants qualified to administer water pollution control programs and conduct or supervise wastewater surveys and treatability studies. However, smaller industries cannot afford an internal staff of pollution control experts and they must turn to consulting firms, universities and colleges, regulatory agencies, and other organizations involved in water pollution control for assistance. Care must be exercised in choosing a consulting engineer since all engineering firms are not equipped to perform or supervise treatability studies.

TABLE 21

SUMMARY, PERSONNEL REQUIREMENTS FOR A 24-HR. WORKDAY

| | Operators, Laboratory Technicians, Maintenance, Instrumentation, and Controls | | | Supervisor | Total | Flow |
|---|---|---|---|---|---|---|
| | Primary Treatment FTE* | Secondary Treatment FTE | Sludge Handling FTE | FTE | FTE | MGD |
| Refinery #1 (Combined Chemical) | 1.03 | 4.08 | - | 1.30 | 6.41 | 15.60 |
| Refinery #2 | 1.79 | - | 0.47 | 0.49 | 2.75 | 3.02 |
| Refinery #3 | 2.05 | 1.45 | 0.35 | 0.92 | 4.77 | 4.61 |
| Refinery #4 | 11.75 | 9.70 | 0.50 | 2.70 | 24.65 | 6.05 |

* Full-Time Equivalents

TABLE 22

TASK FUNCTIONS AND EDUCATIONAL EXPERIENCE NECESSARY FOR EFFECTIVE OPERATION OF POLLUTION CONTROL PROGRAM

| Area | Task Function | Definition of Task | Formal Education Reqd. | Specialized Training Reqd. |
|---|---|---|---|---|
| I Operations | a. Unskilled | Routine operations | Less than H.S.* | On the Job |
| | b. Skilled | Process control; intermediate decision making | H.S.* or more | Operator Training |
| II Laboratory | a. Technician | Routine analysis | H.S.* | On the Job |
| | b. Detailed analysis and plant control | Calculations and evaluations | College or Equal | Short courses |
| III Maintenance | a. Unskilled | Routine maintenance | Less than H.S.* | On the Job |
| | b. Skilled repair | Repair and replacement of complex equipment | H.S.* plus apprentice experience | Short courses |
| IV Instrument and Controls | a. Routine | Routine cleaning, reading and maintenance of instruments | H.S.* | Special Short Courses |
| | b. Operations and Controls | Installation and maintenance of complex instruments and controls | 2-Year Technical School | Special Manufacturers' Courses |

TABLE 22 (Cont)

## TASK FUNCTIONS AND EDUCATIONAL EXPERIENCE NECESSARY FOR EFFECTIVE OPERATION OF POLLUTION CONTROL PROGRAM

| | Area | Task Function | Definition of Task | Formal Education Reqd. | Specialized Training Reqd. |
|---|---|---|---|---|---|
| V | Supervision (operations) | a. Para-professional | Shift operations foreman | H.S.* plus | Operators training school |
| | | b. Professional | Runs plant with broad decision-making ability | College, additional specialized schools and/or masters degree | Short courses, FWPCA courses, industrial managerial and technical courses |
| | | c. Managerial | Runs sanitary district or industrial utility department | College and specialized courses | Specialized courses |

* High School

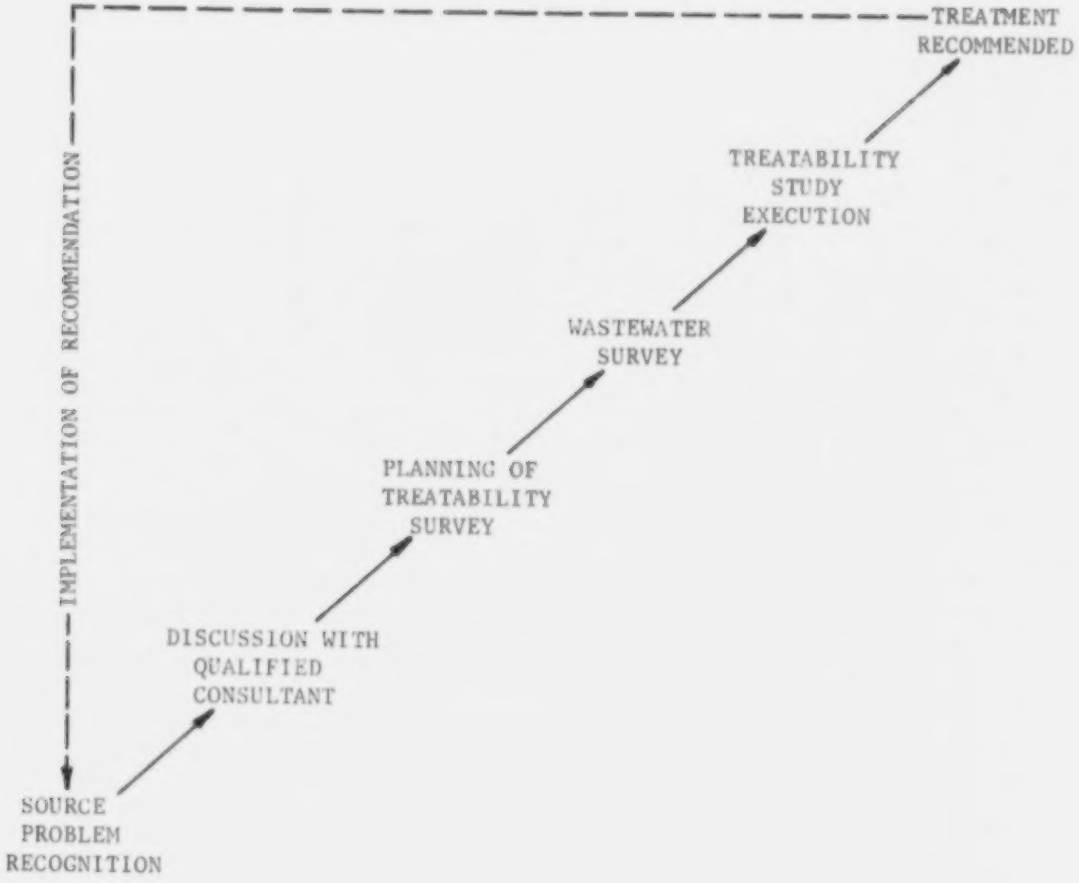
TREATMENT RECOMMENDED
TREATABILITY STUDY EXECUTION
WASTEWATER SURVEY
PLANNING OF TREATABILITY SURVEY
DISCUSSION WITH QUALIFIED CONSULTANT
SOURCE PROBLEM RECOGNITION
IMPLEMENTATION OF RECOMMENDATION

FIGURE 38

SEQUENCE OF EVENTS IN A TREATABILITY STUDY

Many of the tasks related to a treatability study may be accomplished by the industry's personnel and if sufficient equipment and space are available, the consultant may need only to supervise the study and translate the data into design criteria. The industry must fully understand the time requirements and competence levels required to complete the study and this understanding should be reflected in the man-hours allotted to in-house personnel involved in the study. Delays in the treatability study phase will lead to delays in design and construction and could precipitate problems with the local citizenry or regulatory agencies.

The university graduate student specializing in water resources or pollution control represents a valuable source of manpower for industry.

An estimate of treatability study time requirements is presented in Table 23. Data shown in the table have been developed from actual studies of refinery wastewater conducted by a private consulting firm (Engineering-Science, Inc./Texas, 1970). The time requirements have been categorized by task and presented with respect to wastewater flow and refinery capacity.

Many factors may affect the time required to complete a task related to the treatability study. For instance, should a pilot scale plant be incorporated into the study, additional time will be required for construction and operation of the unit. A suitable acclimation period will be required before meaningful operation data may be collected from a biological pilot plant. But, on the other hand, acclimation would not be required should a physical or chemical treatment process unit be utilized.

## TRENDS IN TRAINING

The critical shortage of personnel trained in the field of wastewater treatment has resulted in many state and local agencies conducting water pollution on-the-job training courses.

A formal apprentice program has been established in California by the Orange County Sanitation District (Harper, 1969). This program was designed to train and develop personnel to operate and maintain wastewater treatment and disposal facilities. The program has been established for high school graduates 25 years old and younger, and consists of 2 batterys of 2 years each. The first 2 years consist of familiarization of the trainee with the overall treatment plant operation, and the second phase consists of developing the special skills necessary to understand the mechanisms of wastewater treatment.

A recently completed study of pollution control personnel requirements suggested that the acquisition of competent manpower

TABLE 23

## MINIMUM TIME REQUIREMENTS FOR COMPLETION OF ALL TASKS IN TREATABILITY STUDIES

(Full-Time Man-Day Equivalents)

| Industry Size | | Tasks | | | | |
|---|---|---|---|---|---|---|
| Waste-water Flow (MGD) | (1,000 bbl/day) | Waste water Survey | Waste water Character-ization | In-Plant Consid-eration | Treat ability Study | Total Man-Day Equiva-lents Req'd. |
| 0.4 | 10 | 8.0 | 20.0 | 8.0 | 60 | 96 |
| 0.4-2.8 | 10-49 | 16.0 | 20.0 | 8.0 | 80 | 124 |
| 2.8-5.0 | 50-100 | 16.0 | 40.0 | 20.0 | 120 | 196 |
| 5.0 | 100 | 40.0 | 120.0 | 28.0 | 200 | 388 |

depends on the following 3 related factors (U. S. Senate, 1969):

1. availability of adequate training opportunities;
2. the establishment of higher pay, advancement opportunities, increase in job prestige; and,
3. determination of whether mandatory operation certification is necessary and feasible.

As a result of this study, the Federal government is now actively supporting many training programs in cooperation with governmental units, educational institutions and other organizations to provide facilities to support Item 1 listed above.

## COSTS OF WASTEWATER TREATABILITY STUDIES

Between 1962 and 1967, $36.8 millions were spent for wastewater treatment facilities in the oil refinery industry and it is estimated that an additional $34 million will be spent on improvements to refinery wastewater treatment facilities during the period 1967 through 1970. It is estimated that it would cost in excess of $156 million to replace the existing wastewater treatment facilities in the oil refinery industry alone ("Report on Air and Water Conservation Expenditures of the Petroleum Industry in the U.S.," 1968; Anon, 1968).

The cost of removing approximately 85 percent of the BOD from wastewaters presently discharged from organic chemicals industry has been estimated from $228 million to $341 million for the year 1970 (Projected Wastewater Treatment Costs in the Organic Chemicals Industry, Rice and Company, 1968). The present level of waste treatment expenditures were not cited. It should be noted, however, that the production and sales of organic chemicals are expected to increase approximately 52 percent over the 1968 production level by the year 1973 (Petrochemical Effluents Treatment Practices, Report No. 12020 - 2/70, FWQA). Based on the implementation of more stringent water effluent criteria, the cost of treating the increased wastewater discharges will climb accordingly.

Comprehensive treatability studies conducted by well-trained competent personnel can provide optimum process design information resulting in plant construction economy. Obviously, the successful implementation of the overall water pollution control program requires a treatability study of sufficient scope to investigate several alternatives, the number of which will depend upon the complexity and number of plant waste streams.

Recent trends indicate that present emphasis on low substrate limited biological treatment will be shifted to high rate non-substrate limited processes, requiring physical-chemical means of wastewater treatment in the future. The use of physical-chemical methods is primarily predicated on the trend toward reduced land requirements and provisions for increased treatment efficiency. However, biological secondary treatment combined with tertiary treatment, where required, will continue to be the most economical solution for the majority of petrochemical and refinery wastewater treatment problems.

The City of Cleveland, Ohio, has decided to investigate the feasibility of providing wastewater treatment through the use of physical and chemical processes. This approach has been dictated by the unavailability of additional land for plant improvements needed for secondary biological treatment of domestic wastewaters which presently receive only primary treatment. In the case of Cleveland, real estate constraints rather than biodegradability limitations have influenced the particular design approach.

In contrast, a pilot-sized biological treatment facility has been constructed to investigate the feasibility of treating the combined wastewater flows of more than 14 industries located along the Delaware

River. The pilot plant design was preceded by bench scale treatability studies, the results of which indicated that biological treatment was possible and the treated effluent would meet present criteria. Based on the magnitude of the project, a pilot plant, hydraulically designed for 50 gpm, was constructed using the bench scale data in the design formulation. The treatability study approach applied on a bench scale was repeated using the pilot plant in order to confirm and refine bench scale data as well as to determine and evaluate operational problems, system response to operating and environmental variations, and effluent quality. This study is being financed jointly by the participating industries and the Environmental Protection Agency (Project No. 11060-DRO). The Delaware River Basin Commission is the administering agency and Engineering-Science, Inc., is the project engineering company (Engineering-Science, 1969).

The aforementioned examples demonstrate the need for treatability studies prior to the design of wastewater treatment facilities. Biological treatment should be investigated initially, but the unavailability of land and/or the characteristics of the wastewater may dictate the use of alternate treatment processes. This discussion alludes to the necessity of long-range pollution control planning and the conjunctive implementation of treatability studies and in-plant optimization of water use and product recovery which should result in a net savings in pollution control equipment.

Estimated costs for conducting treatability studies as discussed in this section are presented with regard to wastewater analyses, personnel requirements, and plant wastewater flows.

## WASTEWATER ANALYSES

Numerous analyses are required for wastewater characterization and effective monitoring of bench or pilot scale treating units. These analyses may be limited to pH, dissolved oxygen, oxidation-reduction potential, and TOC in the case of judging the performance of a model waste stabilization pond. They may include organic analyses such as TOD, COD, $BOD_5$, oxygen uptake, spectroscopy, chromatography, volatile solids, *etc.*, in the case of monitoring the removal of petrochemical contaminants in a pilot-activated sludge plant. It is not practical for many industries to maintain elaborate laboratory facilities equipped to perform all analyses needed in a treatability study, and it has been common practice to subcontract all or a portion of the laboratory work to dependable commercial laboratories.

The costs for laboratory services will vary from place to place, and the unit costs are normally dependent upon the number of analyses requested. A typical schedule of average laboratory unit costs as obtained from several commercial laboratories is presented in Table 24. Special discounts are normally available for contract work or where a large number of samples are submitted for analysis. In medium to large surveys where the number of analyses run into the hundreds and thousands, the unit costs may be decreased to less than one-tenth of that shown in Table 24.

## TABLE 24

## COSTS OF CHEMICAL ANALYSES OF WASTEWATERS

| Analysis | Cost Per Analysis |
|---|---|
| Immediate Oxygen Demand | $ 10.00 |
| Biochemical Oxygen Demand, 5-Day | 15.00 |
| Biochemical Oxygen Demand, 20-Day | 20.00 |
| Chemical Oxygen Demand | 15.00 |
| Total Organic Carbon | 10.00 |
| Ammonia Nitrogen | 4.00 |
| Nitrite Nitrogen | 4.00 |
| Nitrate Nitrogen | 4.00 |
| Total Kjeldahl Nitrogen | 30.00 |
| Suspended Solids $10.00, Plus Volatile | 12.50 |
| Total Solids $10.00, Plus Volatile | 12.50 |
| Settleable Solids | 2.00 |
| pH | 1.00 |
| Chloride | 4.00 |
| Sulfate | 4.00 |
| Phosphate | 5.00 |
| Hardness | 4.00 |
| Color, Water Method | 3.00 |
| Color, Wastewater Method | 25.00 |
| Turbidity | 2.00 |
| Petroleum Extract (Fats - Grease) | 10.00 |
| Alkalinity, Phenolphthalein and Total | 5.00 |
| Most Probable Number | 30.00 |
| Phenol | 15.00 |

## MANPOWER COSTS

Labor costs for conducting treatability studies are difficult to estimate as the number of man days required to fulfill each task of the study is dependent upon the competence level of the personnel and the scope of the study. Labor costs categorized by competence level are presented in Table 25. The widest variation occurs at the highest consultant level ($250 to $500 per day), primarily because of the wide range of experience and ability available at this level. Consultants should be retained only when the pollution problems require special expertise that is not available in the industry or cannot be provided by closely associated personnel. Generalized costs for treatability studies have been estimated based on information presented in Tables 24 and 25 and are shown in Table 26. Information concerned with time and cost requirements for treatability studies is based on "judgement" estimates made by engineers with consulting experience in the refinery and petrochemical industries. Thus, it is felt that this information reflects the general requirements necessary to complete comprehensive studies. However, extreme caution should be taken in applying these overall averages to any particular situation since special problems may increase time requirements at any expertise level.

The additional cost to an industry for a wastewater survey will depend on the number of steps that are necessary to complete the study (Figure 38), using other than in-house personnel.

An estimate of the fraction of treatability costs allocated to labor is presented in Table 27. These data are based on information shown in Table 25 and the costs have been categorized according to wastewater flow.

## COSTS OF PREVIOUS TREATABILITY STUDIES

The total cost of any treatability study depends on the quantity and quality of the wastewater flow, size of the industrial staff associated with the pollution abatement program, length of study, level of experience, competence of personnel contracted to complete the study, and other factors which are unique to each industry. Therefore, it is difficult to predict exact costs of studies performed on a particular wastewater. However, close examination of previously conducted studies may prove helpful in determining costs for future studies.

A tabulation of treatability study costs has been prepared and is presented in Table 28. Costs shown in the Table include laboratory analyses and labor, but are exclusive of profit and overhead. Work covered by these studies included wastewater characterization, biodegradability screening, laboratory-scale biological reactor operations and monitoring of reactor contents, and a final report of the findings and recom-

TABLE 25

## LABOR COSTS INVOLVED IN TREATABILITY STUDIES*

| Classification | Responsibilities | Per Day | Per Hour |
|---|---|---|---|
| 1. Special Consultants | Overall Planning and Consultant to project | $250-500 | $32.50-62.50 |
| 2. Supervising Engineers and Scientists | Overall operation, planning, and analysis | 180-250 | 22.50-32.50 |
| 3. Engineers and Scientists | Detailed planning and analysis | 150-200 | 18.75-25.00 |
| 4. Project Engineers and Scientists | On the job supervision and operation | 100-150 | 12.50-18.75 |
| 5. Specialists | Implementation of operation | 100-150 | 12.50-18.75 |
| 6. Supporting Services | Assists study operator | 50-80 | 6.25-10.00 |

---

* These figures include salary costs and ordinary overhead. Applicable expenses for travel and lodging, communications, report preparation, and printing are reimbursable at actual cost plus 10 to 50 percent.

## TABLE 26

## GENERALIZED COSTS OF TREATABILITY STUDIES[*1]

| Wastewater Flow | Wastewater Survey[2] | Wastewater Characterizations | In-Plant Considerations | Treatability Studies | Total |
|---|---|---|---|---|---|
| 0.4 MGD | 850 | 3000 | 850 | 9700 | 14,400 |
| 0.4-2.8 MGD | 2400 | 3000 | 1200 | 12,000 | 18,500 |
| 2.8-5.0 MGD | 2400 | 6000 | 3000 | 18,000 | 29,400 |
| 5.0 MGD | 6000 | 18,000 | 4200 | 32,000 | 60,000 |

---

[*1] Average personnel cost taken as $150/day. Costs exclude purchase of special equipment.

[2] Survey of major streams only.

* * * * * * * * *

## TABLE 27

## FRACTION OF COST PAID TO PERSONNEL IN TREATABILITY STUDIES

| Classification | Total Cost(Percent of Total) | | | |
|---|---|---|---|---|
| | Wastewater Flow (MGD) | | | |
| | 0.4 | 0.4-2.8 | 2.8-5.0 | 5.0 |
| 1. Special Consultants | 10 | 10 | 10 | 10 |
| 2. Supervising Engineers & Scientists | 5 | 10 | 10 | 20 |
| 3. Project Engineers & Scientists | 40 | 40 | 50 | 50 |
| 4. Specialists | 5 | 10 | 10 | 10 |
| 5. Supporting Services | 40 | 30 | 20 | 10 |

TABLE 28

COSTS OF COMPLETED TREATABILITY STUDIES

| Study Number | Wastewater Classification | Flow (MGD) | Scope of Study | Study Length (months) | Analytical Tabulation Analysis | No. | Project Cost |
|---|---|---|---|---|---|---|---|
| 1 | Organic Chemicals<br>Methanol and Formaldehyde Production | 1.5 | 1. General Wastewater Characterization<br>2. Biological Process Simulation<br>a. Continuous Reactors (Act. Sludge)<br>b. Batch Reactors (Act. Sludge)<br>3. Sludge Settling Analyses<br>4. Oxygen Transfer Analyses | 6 | COD<br>BOD<br>TSS<br>VSS<br>$NH_3$ - N<br>TKN<br>$NO_3$ - N<br>$PO_4$<br>$CH_3OH$<br>Cr | 495<br>190<br>550<br>550<br>40<br>120<br>120<br>100<br>50<br>20 | $ 16,500 |
| 2 | Organic Chemicals<br>Butadiene Olefin, Styrene Production | 1.0 | 1. General Wastewater Characterization<br>2. Biological Process Simulation<br>a. Continuous Reactors (Act. Sludge)<br>b. Continuous Reactors (Waste Stabilization Ponds)<br>3. Sludge Settling Analyses<br>4. Oxygen Transfer Analyses<br>5. Microscopic Analyses<br>6. Chemical Coagulation Analyses<br>7. Bioassay Analyses | 12 | COD<br>BOD<br>TOC<br>TSS<br>VSS<br>TKN<br>$PO_4$<br>$SO_4$<br>Cl<br>Oils<br>$O_2$ Uptake<br>Photomicrographs | 500<br>360<br>620<br>335<br>215<br>80<br>50<br>60<br>60<br>60<br>160<br>20 | $ 19,300 |

TABLE 28 (Cont)

COSTS OF COMPLETED TREATABILITY STUDIES

| Study Number | Wastewater Classification | Flow (MGD) | Scope of Study | Study Length (months) | Analytical Tabulation Analysis | No. | Project Cost |
|---|---|---|---|---|---|---|---|
| 3 | Organic Chemicals<br>Production of 2,4-D and 2,4,5-T | <.5 | 1. General Wastewater Characterization<br>2. Biological Process Simulation<br>a. Continuous Reactors (Act. Sludge)<br>b. Batch Reactors (Act. Sludge)<br>3. Stripping of Volatile Compounds<br>4. Warburg Evaluation<br>5. Oxygen Transfer Analyses<br>6. Sludge Settling Analyses | 3 | COD<br>BOD<br>TSS<br>VSS<br>TKN<br>$O_2$ Uptake<br>Warburg Anal.<br>Optical Density | 150<br>150<br>65<br>65<br>5<br>60<br>2 Runs<br>20 | $ 4,900 |
| 4 | Organic Chemicals | 0.5-1.0 | 1. General Wastewater Characterization<br>2. Biological Process Simulation<br>a. Continuous Reactors (Act. Sludge)<br>b. Continuous Reactors (Waste Stabilization Ponds)<br>c. Batch Reactors (Act. Sludge)<br>3. Oxygen Transfer Analyses<br>4. Chemical Coagulation Analyses | 5 | COD<br>BOD<br>TSS<br>VSS<br>Cl<br>$SO_4$<br>Oils<br>Warburg Anal.<br>IR Spectrograph | 50<br>40<br>40<br>40<br>5<br>5<br>5<br>2 Runs<br>2 Samples | $ 2,500 |
| 5 | Individual and Combined Treatability Studies<br>7 Chemical Plants and 2 Refineries | 25.0 | 1. General Wastewater Characterization<br>2. Biological Process Simulation Continuous Reactors (Act. Sludge)<br>3. Oxygen Transfer Analyses | 8 | COD<br>BOD<br>TOC<br>TSS<br>VSS<br>TKN | 700<br>700<br>700<br>800<br>800<br>250 | $ 58,000 |

## TABLE 28 (Cont)

## COSTS OF COMPLETED TREATABILITY STUDIES

| Study Number | Wastewater Classification | Flow (MGD) | Scope of Study | Study Length (months) | Analytical Tabulation Analysis | No. | Project Cost |
|---|---|---|---|---|---|---|---|
| 5 (cont) | | | 4. Sludge Settling Analyses | | $NO_2$, $NO_3$ | 250 | |
| | | | 5. Chemical Coagulation Analyses | | $PO_4$ | 200 | |
| | | | 6. Neutralization Studies | | Phenols | 200 | |
| | | | | | MBA | 100 | |
| | | | | | Alk/acidity | 120 | |
| | | | | | $O_2$ Uptake | 150 | |
| 6 | Petrochemical Production | <0.5 | 1. General Wastewater Characterization | 4 | COD | 30 | $ 3,500 |
| | | | 2. Ozone Test Series - 8 Test Runs | | TOC | 60 | |
| | | | 3. Warburg Evaluation | | TSS | 10 | |
| | | | 4. Carbon Adsorption Simulation (Batch Reactors) | | VSS | 10 | |
| | | | | | Warburg Anal. | 2 Runs | |
| | | | | | Ozone Test | 8 Runs | |
| | | | | | NaI Titrations | 30 | |
| 7 | Hydrocarbon | <0.1 | 1. General Wastewater Characterization | 3 | TOC | 150 | $ 2,550 |
| | | | 2. Biological Process Simulation | | COD | 30 | |
| | | | a. Batch Reactors (Act. Sludge) | | BOD | 15 | |
| | | | b. Batch Reactors (Aerated Lagoon) | | TSS | 15 | |
| | | | c. Continuous Reactors (Waste Stabilization Ponds) | | VSS | 10 | |
| | | | | | Cl | 40 | |
| | | | | | $SO_4$ | 1 | |
| | | | | | $PO_4$ | 1 | |
| | | | | | Alkalinity | 1 | |
| | | | | | $O_2$ | 6 | |

* Costs Represent Actual Salary and Laboratory Costs Exclusive of Overhead - 1969 Cost Index Overhead and profit ranges from 80 to 130 percent of these costs.

mendations. Only a small portion of the wastewater survey is included as a major portion of this effort is done in-house.

Often treatability studies are combined with the preliminary engineering report which covers the design of one or more process systems. Expenditures presented in Table 28 do not reflect the cost of a preliminary engineering report, although it is customary to recommend specific unit processes based on the treatability studies.

Data presented in Table 28 are representative of studies performed on 5 petrochemical and 2 refinery wastewaters ranging from less than 0.5 mgd to 25 mgd. Additional information germane to the scope of each study such as study duration, type and number of analyses, and general wastewater classification is included for detailed comparisons.

The most complex investigation was that of study number 5 which was concerned with the practicability of treating the combined wastewaters from 7 chemical and 2 refining industries. In contrast, study number 7 consisted of characterizing 2 waste streams and conducting batch reactor treatability investigations.

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27 Abstract

This report compiles, interprets and describes the pertinent aspects of conducting a preliminary wastewater treatability study for the refining and petrochemical industries.

The characterization of wastewaters is the basis from which a treatability study can be developed, and includes locating, analyzing, and interpreting the nature of pollutional sources within a petrochemical or refinery complex.

The treatability study, whether it involves chemical, biological, or physical treatment, must necessarily be programmed to yield definitive information concerning pollutional removal rates, anticipated levels of residual or non-removal rates, anticipated levels of residual or non-removable constituents, and treatment process requirements.

The overall project of evaluating the treatability of a wastewater is predicated on the assimilation of sufficient information from which the optimal selection of treatment processes can be made. Given this objective, along with manpower and cost constraints, any treatability study must be carefully planned and properly implemented. This report has 173 pages, 38 figures, 28 tables and 112 references.

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